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VOL. LIV] *SECTION A* [No. 5

SPECTROSCOPIC PROPERTIES AND SPECIFIC HEATS OF MgO AND NaCl

NOVEMBER 1961

Price Rs. 2 or 3 Sh. *Annual Subscription Rs. 18*

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THE VIBRATIONS OF THE MgO CRYSTAL STRUCTURE AND ITS INFRA-RED ABSORPTION SPECTRUM

Part I. The Results of Experimental Study

By Sir C. V. Raman

(*Memoir No. 127 of the Raman Research Institute, Bangalore-6*)

Received September 15, 1961

1. Introduction

The fundamental questions requiring an answer which arise in relation to the infra-red behaviour of crystals are the following: What is the nature of the vibration spectrum of the atomic nuclei in a crystal? How is this vibration spectrum related to its observed infra-red absorption spectra? What is the mechanism of the reflection and of the absorption of infra-red radiation by crystals? A precise and detailed experimental study of the infra-red behaviour of some crystals of simple structure may be expected to furnish an answer to these questions.

Magnesium oxide crystallises in the cubic system and, if the material is pure, the crystals are transparent and colourless. The structure of MgO is similar to that of rock-salt and is thus very simple. Moreover, the binding forces between the atoms being much stronger and their reduced mass much smaller for MgO than for NaCl, the infra-red absorption of MgO appears in a region much more readily accessible to precise investigation than that of rock-salt. Hence, MgO would be a most appropriate choice of material for a study of the kind referred to above.

A collection of MgO crystals came into the writer's hands many years ago as a gift from the Norton Company of Worcester, Mass., U.S.A. Somewhat later, a single crystal of large size was received by him from A. D. Mackay, Inc. of Broadway, New York. It had long been the intention of the writer to make use of this material for a thorough investigation of the kind envisaged in the foregoing paragraphs. Only recently, however, has the availability at this Institute of an infra-red recording spectrograph by Messrs. Leitz of Wetzlar provided with both NaCl and KBr optics enabled

this desire to be fulfilled. The results of the experimental study made with this instrument are described and discussed in this first part of the memoir. In the subsequent parts of the memoir, their theoretical implications and their further consequences are worked out.

The reflecting power of a freshly cleaved surface of an MgO crystal relative to an aluminium mirror was determined by Burstein, Oberly and Plyler (1948) for the spectral region between 10 μ and 35 μ and the results were presented in a paper published in these *Proceedings* some years ago (*Proc. Ind. Acad. Sci.*, 1948, **28 A,** 388). The same authors also recorded the transmission of infra-red radiation in the wavelength range between 5 μ and 13 μ of five cleavage plates of MgO of thicknesses ranging from 9·2 to 0·9 mm. Graphs showing these five transmission curves (in part) and grouped together were reproduced as a figure in the same paper. As regards the reflecting power of MgO, the work of Burstein, Oberly and Plyler was complete and their results will be made use of and discussed in the present memoir. The position is rather different with reference to their studies of the transmission through MgO. Their work did not reveal all the significant features of the behaviour of MgO in this respect. A full and complete picture of the facts is clearly necessary before it is possible for their real significance to emerge. It was with a view to fill the lacunæ in the published results of Burstein, Oberly and Plyler that the present experimental research was undertaken.

2. SOME GENERAL CONSIDERATIONS

In the spectrographic investigations with cleavage plates, we are interested in determining the percentage of transmission through the plate and of ascertaining the spectral composition of the transmitted radiation and the manner in which it varies with the thickness of the plate. The loss in transmission may be divided into three parts: (*a*) the loss by reflection at the surface of incidence, (*b*) the loss by absorption within the material and (*c*) the loss by reflection at the surface of emergence. The relative proportions of these three losses would evidently vary with the circumstances, including especially the thickness of the plate, as this would determine the magnitude of the true absorption loss. When the reflecting power is large, the three losses would add up and it would become difficult to extricate them from each other and evaluate them separately.

At wavelengths greater than 13 μ, the reflecting power of MgO is small, as was shown by Burstein, Oberly and Plyler and its alteration with

wavelength would therefore not be significant. Hence in the spectral region between 5 μ and 13 μ covered by their studies of the transmission by MgO, the interpretation of the observations presents no particular difficulty. The position is, however, different in the wavelength range between 13 μ and 15 μ in which the reflecting power was shown by Burstein *et al.* to rise steeply from nearly zero to 75%. This rapid increase would make it difficult to determine how the absorption loss within the material varies with wavelength in the same range. However, by making observations with different thicknesses, the existence of a true absorption could be demonstrated. The position would be much more difficult in the wavelength range between 15 μ and 25 μ. The reflecting power in this range is very high and hence the percentage transmission would be small and difficult to determine, unless indeed the plate is itself so thin that the full reflecting power would be unable to manifest itself. Indeed, it is clear that for an elucidation of the infra-red behaviour of MgO in the wavelength range between 15 μ and 25 μ, it would be necessary to work with extremely thin layers of the material, not exceeding a few microns.

A method of obtaining MgO films for the study of their transmission properties which has been frequently employed by the earlier investigators is that of the deposition of the fumes of burning magnesium on a plate transparent to infra-red radiation. It will suffice here to refer to the work of A. O. Momin published in these *Proceedings* in which references to the earlier literature will be found (*Proc. Ind. Acad. Sci.*, 1953, **37 A**, 254). Momin made a series of measurements with fourteen different thicknesses of MgO films prepared by fuming on to a KCl plate from a burning magnesium ribbon. Commencing with an extremely thin layer which was just visible, the thickness was progressively increased by adding more layers of MgO on the same plate by fuming up to a thickness of about 2·4 millimetres when the films begin to break away from the KCl plate. The readings were taken with a single-beam Beckman Model IR 2 infra-red spectrophotometer making point-to-point observations. Four typical graphs which between them cover the whole range of thicknesses employed have been reproduced with Momin's paper. They show some interesting features, but it is quite clear on an inspection of the graphs that they do *not* represent the real transmission curves of MgO at any of the thicknesses used and that on the other hand they depict a complex effect in which the scattering of infra-red radiation in its passage through the optically heterogeneous film produced by the deposition of the fumes and the extinction produced by such scattering play a highly important role.

The spurious and misleading nature of the results given by fumed films of MgO becomes evident when it is remarked that to exhibit an observable transmission in the wavelength range between 15 μ and 25 μ, the thickness of the film cannot exceed a few microns. Films of this order of thickness should be fully transparent in the wavelength range between 1 μ and 13 μ. Actually, Momin's graph for his thinnest film shows a transmission of only 17% at 1 μ. This increases fairly rapidly to 70% at 5 μ and then more slowly to 80% at 13 μ. The optical heterogeneity of the film has thus a notable effect on its transmission up to 13 μ. Hence, to assume that it would cease to influence the behaviour of the film at still greater wavelengths is clearly unjustifiable. The falsity of the assumption is demonstrated by the comparative studies made at this Institute with fumed MgO films and with two other techniques presently to be described. The publications by earlier investigators who have based themselves and their theoretical discussions on the results obtained with fumed MgO films are vitiated by this error and are therefore entirely valueless.

3. METHODS OF THE PRESENT INVESTIGATION

Since MgO crystals exhibit an easy cleavage parallel to the cube faces, it is possible to obtain a whole series of plates suitable for the observation and of various thicknesses ranging from several millimetres down to about a tenth of a millimetre. It is desirable to use a fairly large crystal to start with. The area of the plates detached from it would then be sufficient to make a satisfactory recording of the transmission curves. The cleavage surfaces are not always optically as smooth as could be desired. It is necessary in such cases to grind and polish both the faces to as high a degree of optical perfection as practicable. To obtain plates thinner than about a tenth of a millimetre, two alternative techniques are available. That employed in the present investigation was to grind and polish both faces of a cleavage plate about a millimetre thick to start with and having made observations with it, to grind one of the faces with the finest grade of carborundum abrasive until the thickness is reduced to the extent desired. The ground face is then repolished and the transmission recorded. This process can be repeated and the transmission by plates which are progressively thinner and thinner can be studied until the practical limit to the applicability of the method is reached. This limit is set by the fragility of the material. With plates of fair size, it is possible to reduce the thickness to about 50 microns, while with smaller sizes one can go down to about 20 microns.

An alternative technique is to immerse a cleavage plate in hot concentrated hydrochloric acid and allow the acid to act until the thickness of the plate has been reduced to the desired extent. The defect of this technique is the unsatisfactory nature of the resulting surfaces.

To obtain the extremely thin absorption layers with which one could expect to find an observable transmission in the spectral range between 15 μ and 25 μ, the following technique was adopted in the present investigation. A small fragment of an MgO crystal was reduced to the finest possible state of subdivision by prolonged grinding in an agate mortar. A little of the material thus obtained was stirred up into a thin paste with liquid paraffin. The transmission in the KBr range of the spectrograph by the thinnest possible layer of this paste held between two KBr plates was recorded, the absorption by the paraffin being compensated by a similar layer of the liquid alone held between two KBr plates. As a test of the satisfactory nature of the technique, the transmission in the NaCl range was also recorded.

Another technique which was also adopted was to mix a very small quantity of very finely divided MgO with one gram of finely powdered KBr and to compress the MgO–KBr mixture under high pressure in a vacuum into a flat tablet of which the transmission was recorded. By varying the quantity of MgO which was put into the tablet, the effective absorption path could be increased to the extent desired.

Since the paste and pellet techniques gave very similar results, it was not considered necessary to try out still another possible procedure of obtaining thin films of MgO, *viz.*, that of evaporating the material in a vacuum and depositing it on a suitable support.

4. Review of the Results

The wavelength scale of the recording spectrograph for the NaCl optics covers the range between 1 μ and 15 μ, while with the KBr optics it covers the range between 13 μ and 24 μ. The overlap of the two scales over the range between 13 μ and 15 μ is a useful feature, since it provides a check on the proper functioning of the instrument and as it is also the range over which the reflecting power of MgO increases rapidly from nearly zero to some 75%.

Some 75 spectrographic records were made with the instrument, the majority with the NaCl optics and the rest in the KBr range. Some 25 different cleavage plates of various sizes and thicknesses were employed and numerous records were also obtained with the paste and pellet techniques

already described. Before we proceed to discuss the results in detail, it appears useful to review the general features which emerge from the study, thereby enabling us to get a broad picture of the experimental situation and consider its significance.

The most striking feature exhibited by the records is that the infra-red behaviour of MgO is quite different in the three spectral ranges which we shall refer to as I, II and III respectively. Spectral range I extends from 6μ to 10μ. Spectral range II extends from 10μ to 15μ. Spectral range III extends from 15μ to 24μ. Closely associated with this feature is the fact that the spectral character of the radiation transmitted by MgO depends greatly upon the absorption path. When the cleavage plate is a few millimetres thick, spectral region I exhibits a progressive change from complete transparency at 6μ to complete opacity at 10μ, while spectral regions II and III are completely cut out. If the absorption path is a few tenths of a millimetre, spectral range I is almost completely transmitted and spectral region II exhibits a transmission spectrum with characteristic features, while spectral region III is cut out. If the absorption path is only a few microns, spectral range III exhibits an observable transmission, while spectral region I, is completely transmitted and spectral region II is let through for the most part.

The facts stated above clearly indicate that the infra-red activities which manifest themselves respectively in the spectral regions I, II and III are of very different orders of magnitude. An explanation for this situation which suggests itself is that the same fundamental modes of vibration are responsible for the activities manifested in the three spectral regions, but that we are concerned with the fundamental modes and with their first and their second overtones respectively in the three cases. In other words, the fundamental absorption frequencies manifest themselves in spectral region I, their first harmonics in the spectral region II and their second harmonics in spectral region III. On this basis, the great differences in the strength of the observed absorptions in the three regions would find an immediate explanation.

If what has been suggested above is correct, we should expect to find quantitative relationships between the specific features observed in the spectral regions I, II and III in the recorded transmission curves. We proceed, therefore, to describe and discuss these observed features.

5. SPECTRAL REGION I: 6μ TO 10μ

We may begin with a few remarks on the transmission of infra-red radiation in the wavelength range between 1μ and 5μ by cleavage plates

of MgO. Residual imperfections in the cleavage surfaces are unavoidable. Their effect manifests itself as a diminution in the percentage of the regularly transmitted radiation in the region of the near infra-red. If, however, a large-sized crystal is used and its cleavage is effected with due care, the effect of surface imperfections on the transmission which may be perceptible at 1 μ becomes small at 4 μ and negligible at 5 μ. Transmissions as high as 95% may be obtained at 5 μ.

The region between 5 μ and 6 μ is of particular interest. With a cleavage plate 7·5 millimetres thick, the transmission is observed to diminish by 8% between 5 μ and 6 μ. With a plate thickness of 3 millimetres, the diminution is only 3%, while with a plate thickness of 1·6 millimetres, there is no observable fall of the transmission between 5 μ and 6 μ, the curve running quite horizontally between these wavelengths. It is clear from these observations that while there is a sensible absorption of infra-red radiation between 5 μ and 6 μ, it is extremely weak and of a lower order of magnitude than the absorption between 6 μ and 10 μ which we shall proceed to describe and discuss.

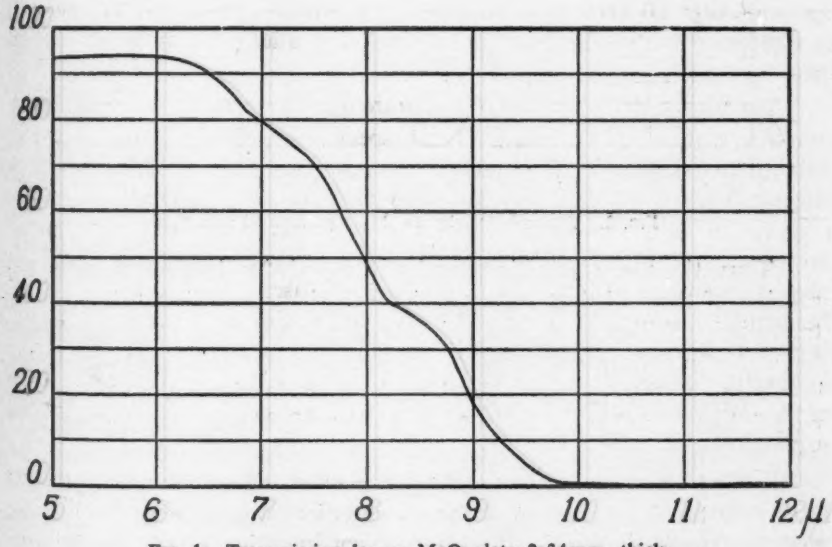

FIG. 1. Transmission by an MgO plate 2·34 mm. thick.

Figure 1 reproduces the record obtained with a cleavage plate 2·34 millimetres thick. We may draw attention here to the following features observed in it. The record runs horizontally between 5 μ and 6 μ. Beyond 6 μ, it dips down and becomes steepest at 6·8 μ. It then takes a sharp turn and

follows a different course in which the wavelength at which the transmission drops most steeply is 7·85 μ. Between 8 μ and 9 μ the curve again changes its course. The slope is rather small at 8·5 μ, beyond which it increases rapidly. The wavelength of steepest descent is 9 μ. Between 9 μ and 10 μ, the curve descends less quickly. Its slope diminishes until finally the curve touches the line of zero transmission at 10 μ. Beyond 10 μ, there is a complete cut-off.

FIG. 2. Transmission by an MgO plate 0·91 mm. thick.

Thus, the spectrographic record of transmission between 6 μ and 10 μ consists of three distinct sectors which exhibit quite different features, the transmission falling most steeply in the three sections at the wavelengths 6·8 μ, 7·85 μ and 9 μ respectively. The three sectors can also be recognised in numerous other records which have been made with various thicknesses, *viz.*, 7·5 mm., 3·0 mm., 1·6 mm., 1·34 mm., 1·04 mm. and 1·00 mm. It has, however, not been thought necessary to reproduce all these records here. That the three sectors exhibit the effect of specific absorptions is shown by the fact that each of them has a distinct absorption strength and that this results in altering the over-all configuration of the graph in the wavelength range between 6 μ and 10 μ when the thickness is increased or diminished. Nevertheless, there is no difficulty in recognising the individual distinctive features described above in every case. In particular, the wavelengths of steepest descent, *viz.*, 6·8 μ, 7·85 μ and 9 μ remain the same in

all the records. Thus, these wavelengths possess a real significance in relation to the absorptive behaviour of MgO.

The wavelengths 6·8 μ, 7·85 μ and 9 μ correspond to infra-red frequencies which expressed in wave-numbers are respectively 1470 cm.$^{-1}$, 1275 cm.$^{-1}$ and 1110 cm.$^{-1}$ Assuming these to be the second overtones of a set of fundamentals, the latter would be 490 cm.$^{-1}$, 425 cm.$^{-1}$ and 370 cm.$^{-1}$ in wave-numbers and 20·40 μ, 23·52 μ and 27·0 μ respectively in wavelengths. The first overtones would then have the frequencies 980 cm.$^{-1}$, 850 cm.$^{-1}$ and 740 cm.$^{-1}$ in wave-numbers and the corresponding wavelengths would be 10·20 μ, 11·76 μ and 13·5 μ. The frequencies of the fourth order would be 1960 cm.$^{-1}$, 1700 cm.$^{-1}$ and 1480 cm.$^{-1}$ and the corresponding wavelengths 5·1 μ, 5·9 μ and 6·8 μ respectively. We give below a table of these frequencies and wavelengths.

TABLE I

Vibrational frequencies and corresponding wavelengths

Order	Frequencies in cm.$^{-1}$	Wavelengths in μ
Fundamental ..	490, 425, 370	20·40, 23·52, 27·0
Octave ..	980, 850, 740	10·20, 11·76, 13·5
Third Harmonic ..	1470, 1275, 1110	6·8, 7·85, 9·0
Fourth Harmonic ..	1960, 1700, 1480	5·1, 5·9, 6·8

The figures listed in Table I enable us immediately to explain various facts already known regarding the infra-red behaviour of MgO. For example, Burstein, Oberly and Plyler had observed that the reflecting power of MgO determined and represented graphically is highest in the wavelength region between 20 μ and 24 μ. We notice that this region includes the first two fundamental wavelengths shown in Table I. Then again, Burstein, Oberly and Plyler had noticed that in the transmission curves of MgO plates which were less than a millimetre thick, two well-defined absorption maxima appear whose wavelengths were given by them as 10·19 μ and 11·82 μ. These may be identified as the first two wavelengths of the octave series shown in Table I. The fact mentioned earlier in the present memoir, that there is an extremely weak infra-red absorption between 5 μ and 6 μ is also satisfactorily explained, since the first two wavelengths shown as the fourth harmonics in Table I fall within this range.

Thus, what is already known regarding the infra-red behaviour of MgO provides us with ample justification for accepting the basic idea which was put forward above and making use of it in interpreting the fresh experimental data which emerge from the present investigation.

6. SPECTRAL REGION II: 10 μ TO 15 μ

That the infra-red absorption appearing between 6 μ and 10 μ is of a higher order than that manifested between 10 μ and 15 μ is clearly proved by various facts of observation. In the first place, there is a total cut-off between 10 μ and 15 μ unless the absorption paths are used are much smaller than those which are required to exhibit any sensible absorption in the 6 μ to 10 μ region. Then again, when such smaller thicknesses are used, the transmission is observed to be nearly complete over the range between 6 μ and 10 μ; in these circumstances also, a steep fall is observed in the transmission curve near 10 μ which is the dividing boundary between spectral ranges I and II (*see* Figs. 2, 3, 4 and 5).

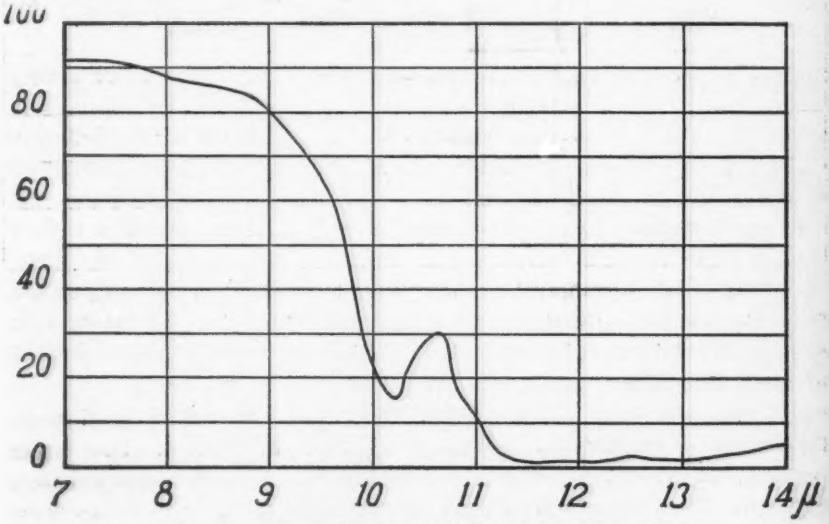

FIG. 3. Transmission by an MgO plate 0·30 mm. thick.

On the long-wave side of the boundary between spectral regions I and II, the characteristic absorption at 10·20 μ first clearly makes its appearance when the absorption path is rather less than one millimetre. This absorption evidently represents the octave of the highest fundamental frequency of vibration of the crystal structure of MgO. As the absorption path is

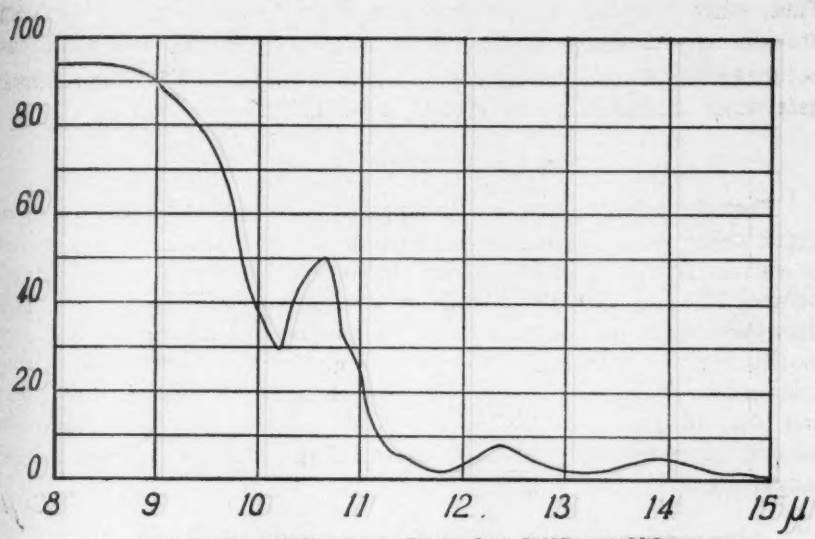

FIG. 4. Transmission by an MgO plate 0·128 mm. thick.

progressively diminished, this absorption emerges more and more clearly from its background and become a very striking feature of the transmission curves. Its initial appearance is shown in Fig. 2 which was recorded with a cleavage plate 0·91 mm. thick. A later stage in which the absorption at 10·20 μ is very prominent and exhibits its characteristic sharpness and V-shaped configuration is represented in Fig. 3 above recorded with a cleavage plate 0·30 mm. thick. With diminishing thickness of the plate, the V-shaped dip in transmission retains both its sharpness and its position on the wavelength scale at 10·20 μ but moves upwards in the figure, as is to be expected from the diminishing strength of the absorption which it represents (*see* Figs. 4, 5, 6, 7, 8 and 9).

The second minimum of transmission located at 11·76 μ and shown in Table I as an octave of a fundamental mode makes its appearance rather inconspicuously in Fig. 3. But as the thickness of the plate is progressively diminished, it becomes more and more conspicuous, as will be seen from the series of records, until it becomes even more conspicuous than the minimum at 10·20 μ (Figs. 4, 5, 6, 7 and 8). Like the minimum at 10·20 μ, the minimum at 11·76 μ retains its position on the wavelength scale but moves upwards as the absorption path is diminished.

Referring to the spectrographic records reproduced as Figs. 4, 5 and 6, we find that in each of them, the transmission reaches a maximum at about

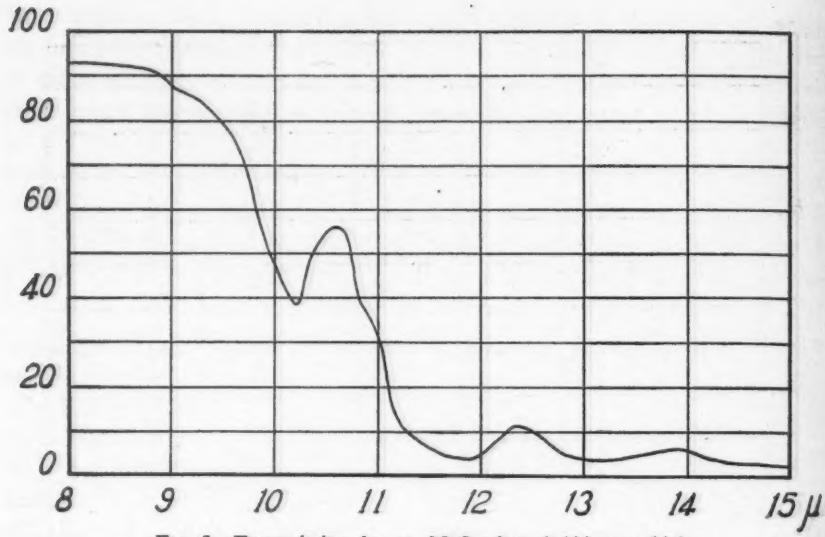

FIG. 5. Transmission by an MgO plate 0·114 mm. thick.

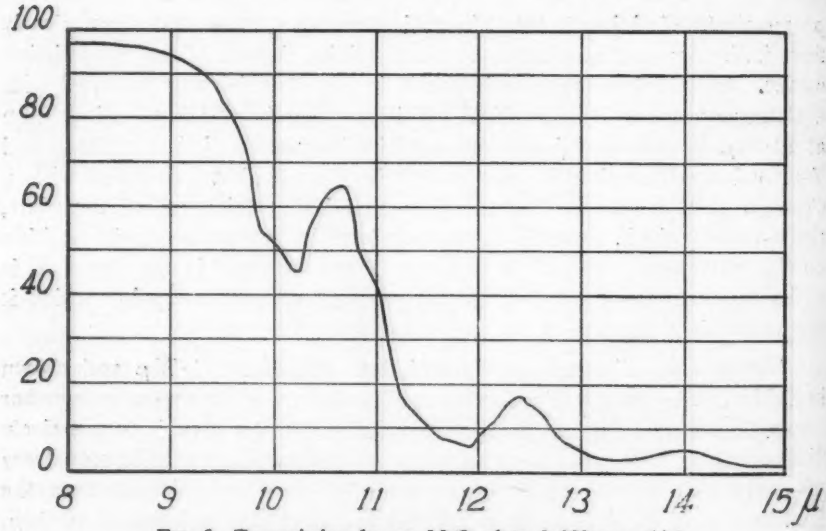

FIG. 6. Transmission by an MgO plate 0·088 mm. thick.

12·4 μ and then drops down to a much lower value at about 13·3 μ. The actual transmission at 13·3 μ is small in Fig. 4 and is distinctly larger in Figs. 5 and 6. That there is a real absorption at 12·4 μ and that this goes

up to a much higher value at 13·3 μ is thus abundantly clear. We are therefore justified in stating that there is a minimum of transmission at about the wavelength 13·5 μ which was listed in Table I as the third in the series of octaves. The reason why the existence of this minimum is not made more conspicuous by a progressive rise of the curve in the region between 13·5 μ and 15 μ with diminishing thickness is to be found in the enormous increase in the reflecting power of MgO which occurs in the same region of wavelength. The fall in transmission arising therefrom more than sets off the increase in the transmission due to the diminishing thickness of absorbing material.

That the percentage transmission through a plate of MgO in the wavelength region between 13·7 μ and 15 μ is almost entirely determined by the reflection losses is evident on a comparison of the records for this region appearing in Figs. 8 and 9 below. The absorbing path in the two cases was respectively 57 microns and 21 microns. It will be noticed that in spite of this great difference in the thickness of the absorbing material, the percentage transmission between 13·7 μ and 15 μ remains substantially unaltered, whereas between 12 μ and 13·7 μ, it has increased enormously.

Thus, the inference from the observations made in spectral region I that three absorptions which we now locate at 10·20 μ, 11·82 μ and 13·7 μ respectively should appear in spectral region II is abundantly confirmed by the actual facts of observation. The conclusion follows irresistibly that the MgO crystal structure has the three fundamental modes of vibration with the respective frequencies which have been listed in Table I.

7. Spectral Region III: 15 μ to 24 μ

The techniques used to study the transmission in this region using the KBr optics have already been explained. Figure 10 shows two transmission records obtained with the paste technique: the upper of the two curves was obtained without any spacer to hold apart the two KBr plates between which the thin film of paraffin containing the finely divided MgO was located. The thickness of the film was hence the very smallest possible and presumably of the same order of magnitude as the size of the MgO particles contained in it. The second record in the figure was with a spacer 30 microns thick separating the two KBr plates. The two records reproduced in Fig. 11 are those recorded with NaCl optics for the wavelength region between 8 μ and 15 μ in the same two cases. We shall return presently to a consideration of the features appearing in Figs. 10 and 11.

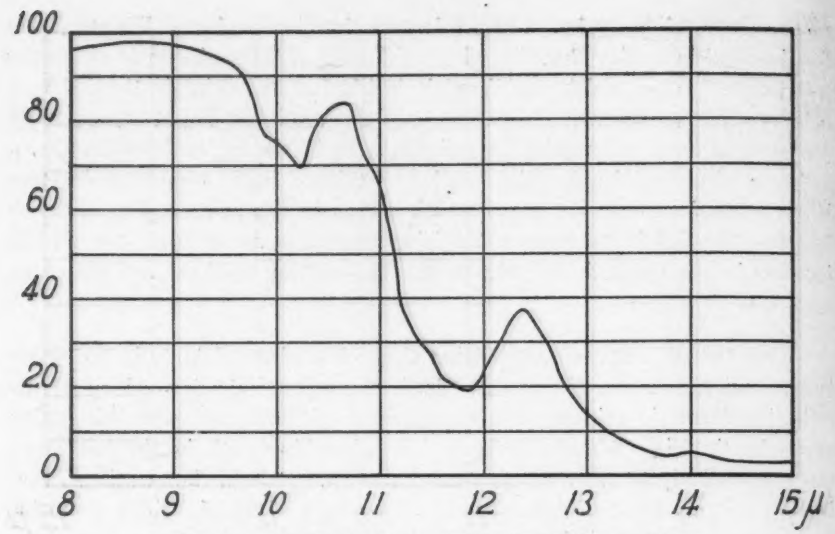

FIG. 7. Transmission by an MgO plate 0·06 mm. thick.

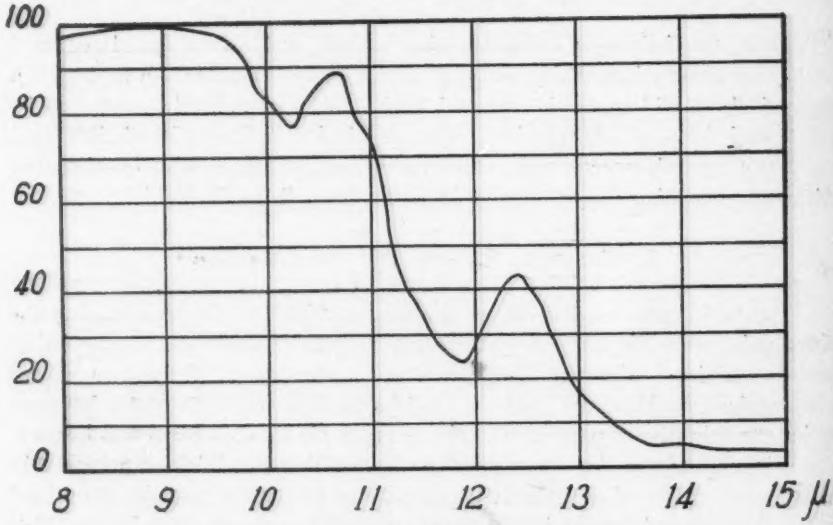

FIG. 8. Transmission by an MgO plate 0·057 mm. thick.

Figure 12 below reproduces four records for the KBr range of the spectrograph obtained with the pellet technique already described. The pellet was a circular disc of 1 centimetre radius containing one gram of KBr and

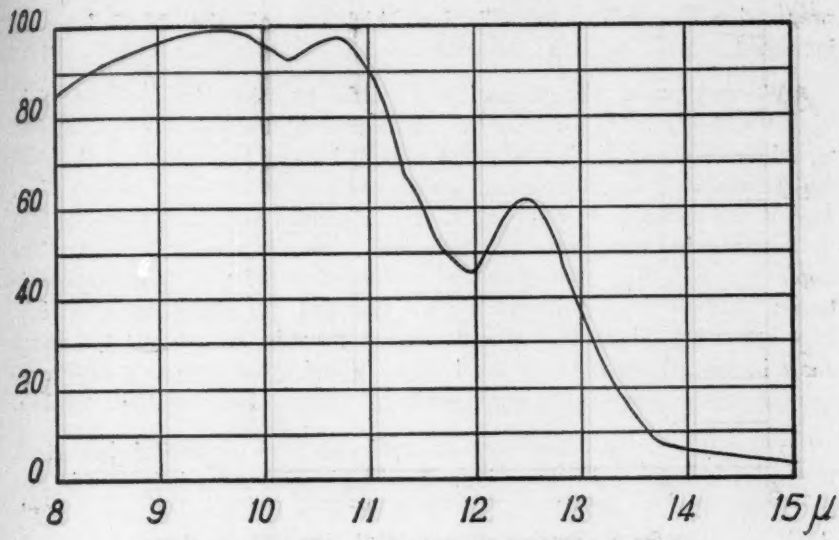

FIG. 9. Transmission by an MgO plate 0·021 mm. thick.

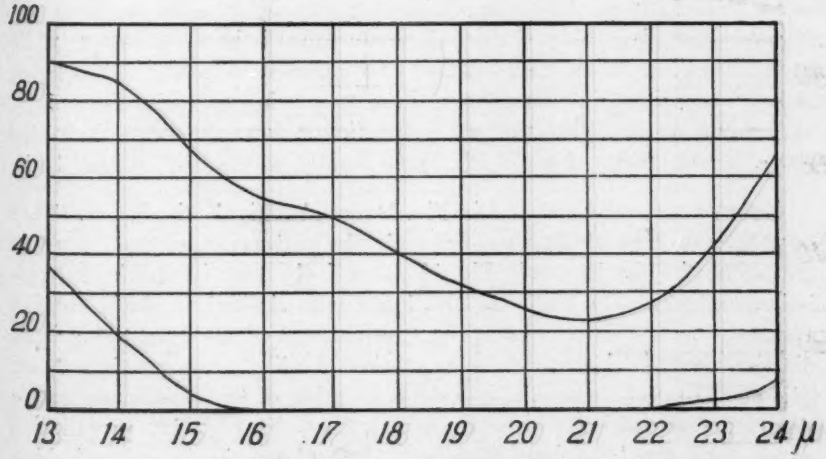

FIG. 10. Transmission curve of MgO films (Paste Technique).

four different quantities of finely divided MgO, *viz.*, 1 milligram, 1·2 milligrams, 2 milligrams and 5 milligrams respectively. The effective absorption paths through MgO would thus be respectively in the four cases 3·2 μ, 3·8 μ, 6·4 μ and 16 μ. As is to be expected, the four figures exhibit a rapid and

progressive change as the effective thickness of the MgO layer is increased.

We may make the following remarks on the data presented in Figs. 10, 11 and 12. It is evident that the results obtained with the two different techniques are very similar and that they fit into each other perfectly when the differences in the effective absorption paths are taken into consideration. Indeed, the curves in Figs. 10 and 12 form a regular sequence showing how the transmission alters with a progressive increase in absorption path. The upper curve in Fig. 10 represents the behaviour of the thinnest possible layer; the first three curves in Fig. 12 represent the subsequent alterations with increasing thickness, while the second curve in Fig. 10 and the fourth curve in Fig. 12 represent the final stages in which the layers are practically opaque to all radiations in the wavelength region between 15μ and 24μ.

The first of the two curves reproduced in Fig. 10 is particularly important. It depicts the absorptive behaviour of an MgO film when it is so thin that the losses due to reflection at its two surfaces can be disregarded. It is significant that the absorption is greatest at about 21μ and falls off quickly at greater wavelengths. This is the behaviour which we might expect to observe if the fundamental mode of highest frequency of which the characteristic wavelength is $20{\cdot}40\mu$ is the only mode which is infra-red active, while that the numerous other modes whose characteristic wavelengths are larger and have been listed in Table I are either totally inactive or active only in a very minor degree. The shift of the maximum from the theoretical value $20{\cdot}40\mu$ to the observed value of 21μ is readily understood on that basis.

The two curves reproduced in Fig. 11 are also highly significant. They show that the films studied were completely transparent at 8μ. The two upper curves in Fig. 10 and in Fig. 11 respectively agree in showing a transmission of 90% at 13μ while the two lower ones similarly agree in showing a transmission of 35% at 13μ. The transparency of the films at 8μ is an indication that the losses due to scattering at all greater wavelengths are negligible. In other words, it is a demonstration of the satisfactory nature of the technique employed. In this respect, the results provide a very striking contrast with the behaviour of fumed MgO films. As has already been remarked, the fumed MgO films exhibit the effect of scattering very markedly. Hence the results obtained with them are erroneous and totally misleading.

We may also remark on a feature shown by the upper curve in Fig. 10 and also by the two upper curves in Fig. 12, *viz.*, the downward bulge of the transmission curve in the region of wavelengths between 15μ and 17μ.

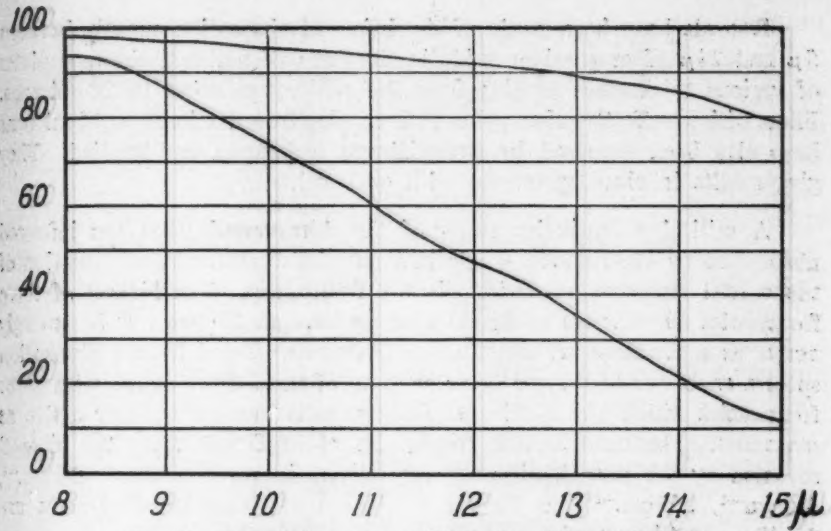

FIG. 11. Transmission curve of MgO films (Paste Technique).

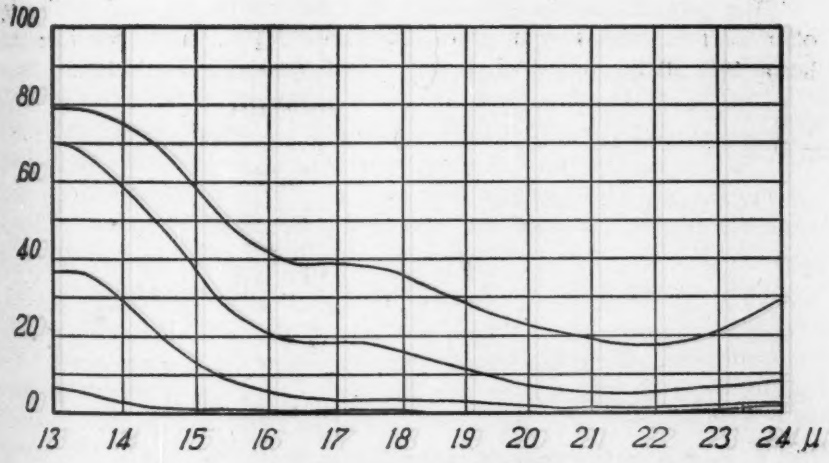

FIG. 12. Transmission curve of MgO films (Pellet Technique).

This is a clear indication that there is a specific absorption which we shall locate at 16 μ and which is clearly the octave of still another fundamental mode whose characteristic wavelength is 32 μ and characteristic frequency is therefore 313 cm.$^{-1}$

8. SUMMARY

Records have been made of the infra-red absorption spectra between 5μ and 24μ of magnesium oxide in the form of polished cleavage plates of various thicknesses ranging from 7·5 millimetres down to 20 microns. Films with an effective absorption path ranging from 1 micron to 16 microns have also been prepared by two different techniques and studied. They give results in close agreement with each other.

A critical comparative study of the data reveals that the infra-red absorption by MgO has its origin in a set of distinct modes of vibration of the crystal structure possessing discrete frequencies. The highest of these frequencies corresponds to an infra-red wavelength $20{\cdot}40\mu$. It is strongly active as a fundamental and also as overtones. The infra-red absorption spectra enable us to recognize the presence of three other modes with lower frequencies which are inactive as fundamentals but are strongly active as overtones. The characteristic frequencies of MgO (including the highest) revealed by the investigation are respectively in wave-numbers 490 cm.$^{-1}$, 423 cm.$^{-1}$, 365 cm.$^{-1}$ and 313 cm.$^{-1}$ The corresponding wavelengths are $20{\cdot}40\mu$, $23{\cdot}64\mu$, $27{\cdot}4\mu$ and 32μ.

The present investigation shows that the results reported earlier by other authors which were obtained with fumed MgO films are spurious and hence that all theoretical discussions based thereon are valueless.

THE VIBRATIONS OF THE MgO CRYSTAL STRUCTURE AND ITS INFRA-RED ABSORPTION SPECTRUM

Part II. Dynamical Theory

By Sir C. V. Raman

(*Memoir No. 127 of the Raman Research Institute, Bangalore-6*)

Received September 15, 1961

1. Introduction

The fundamental property of the atomic structure of a crystal is that it comes into coincidence with itself following a unit translation along any one of the three axes of the lattice. Hence the normal modes of atomic vibration characteristic of the structure of a crystal should satisfy a similar requirement, in other words, they should remain unaltered following such a unit translation. From this, it follows that the atomic modes of vibration satisfy the following rule: in any normal mode, equivalent atoms in the structure have *either* the same amplitude and the same phase, *or* the same amplitude but alternating phases, along the axes of the lattice. In the MgO structure, we have two interpenetrating face-centred cubic lattices of Mg and O atoms respectively. Applying the rule stated, it should be possible to deduce the normal modes of vibration of this structure purely from symmetry considerations. One could also go further and obtain explicit formulæ for the frequencies of the normal modes in terms of the interatomic force-constants. We shall, in what follows, carry out the programme here indicated.

2. Vibrations of a Face-Centred Cubic Lattice

The three unit translations in a face-centred cubic lattice are parallel to the three edges of the primitive rhombohedral cell of the lattice. These edges are found by joining an atom at a cube corner with the three atoms at the centres of the three adjoining cube faces. The various modes of normal vibration of the lattice given by the rule stated above are found by choosing one or another of the eight possible combinations of the phases of these three atoms relative to the phase of the atom at the cube corner and continuing the scheme to the more distant atoms in the lattice. It is then found that the possible modes of vibration may be described *either* as movements of the cubic planes of atoms in the crystal *or* as movements of the

octahedral planes of atoms; in either case, the alternation of phase along an axis results in the alternate planes of one or the other species moving in opposite phases. Since we have three sets of cubic planes and four sets of octahedral planes, the movements of these planes normal to themselves would give three and four normal modes respectively, but only two distinct frequencies. We have also to consider the movements of the planes parallel to themselves, and as there are two possible directions of movement in each case, we obtain six and eight such normal modes respectively, but here again only two additional frequencies by reason of the symmetry of the crystal. Thus, in all, we have only four distinct frequencies of vibration. In the foregoing we left out of consideration the case in which the phases of movement of the three atoms at the face-centres and of the atom at the cube corner are the same. This corresponds to a simple translation of the unit rhombohedral cell carrying eight atoms at its corners. The 24 degrees of freedom of movement of these eight atoms are thus distributed as follows amongst the possible movements of the lattice.

TABLE I

	Degeneracy
Vibrations of the cubic planes normal to themselves ..	3
Vibrations of the cubic planes tangential to themselves ..	6
Vibrations of the octahedral planes normal to themselves ..	4
Vibrations of the octahedral planes tangential to themselves ..	8
Translations of the unit cell	3
Total degrees of freedom	24

3. THE VIBRATIONS OF THE MgO STRUCTURE

In the MgO crystal, the Mg and O atoms occupy the points of two similar face-centred cubic lattices interpenetrating each other. These are so disposed that each Mg atom is surrounded by six equidistant O atoms, and each O atom is surrounded by six equivalent Mg atoms. In the cubic planes of the structure the Mg and O atoms appear together, while in the octahedral planes they appear separately but in equidistant planes, each plane of Mg atoms having two planes of O atoms and each plane of O atoms having two planes of Mg atoms situated symmetrically on either side of it.

This arrangement has interesting consequences regarding the possible vibrational modes of the structure, as we shall presently see.

Table I would represent equally well the schemes of vibration of the Mg atoms and of the O atoms. Hence, the interactions of these atoms with each other would result in a modification of the frequencies of vibration without altering the geometry of the modes. Since the cubic planes contain both Mg and O atoms, each of their movements would split into two modes: in one of the two modes, the Mg and O atoms in a cubic plane would oscillate in the same phase and in the other they would oscillate in opposite phases. The situation would be a little different with respect to the atomic layers parallel to the octahedral faces. In view of the disposition of Mg and O atoms in these layers, it is evident that the oscillations of Mg and O layers would occur independently of each other, the Mg planes remaining at rest when the O planes oscillate and *vice versa*. The three translations of the unit cells would also split into two. The movement of the Mg and O atoms in opposite phases would give a triply degenerate normal mode, while their movement in the same phases would represent a residuum of three translations.

Thus, the structure would have only nine different frequencies of vibration, while the number of normal modes would be 45 which together with the residuum of the three translations would account for the 48 degrees of freedom of movement of 8 atoms of magnesium and 8 atoms of oxygen when added together. The description of the modes of vibration corresponding to each of the nine different frequencies is entered in the second column of Table II, while their respective degeneracies are shown in the third column of the table. These degeneracies are the same as shown in Table I, but they now total up to 48 instead of to 24 as in the former table.

The modes have been shown in the first column of Table II in the order of the magnitude of their respective frequencies suggested by the approximate formulæ of the dynamical theory to be given presently. But this arrangement is subject to revision on the basis of a more accurate evaluation of those frequencies. It will be noticed that at the top of the table listed as mode I appears the triply degenerate oscillation of the Mg and O atoms in the structure moving against each other in opposition of phase. It will also be noticed that next to it in the descending order of frequency appear the tangential and normal modes of oscillation of the cubic layers of atoms. These are listed in the table as modes II and III, while two other modes of oscillation of the cubic layers in which the phases of movement of the Mg

TABLE II

Sl. No.	Description of Mode	Degeneracy
I	Oscillation of the Mg and O atoms in opposite phases ..	3
II	Tangential oscillations of the cubic planes, Mg and O atoms having opposite phases	6
III	Normal oscillations of the cubic planes, Mg and O atoms having same phases	3
IV	Normal oscillations of the octahedral planes of O atoms	4
V	Tangential oscillations of the octahedral planes of O atoms	8
VI	Normal oscillations of the octahedral planes of Mg atoms	4
VII	Tangential oscillations of the octahedral planes of Mg atoms	8
VIII	Normal oscillations of the cubic planes, Mg and O atoms having opposite phases	3
IX	Tangential oscillations of the cubic planes, Mg and O atoms having same phases	6
X	Translations	3
	Total degrees of freedom	48

and O atoms are different appear at the bottom of the table as VIII and IX respectively. The oscillations of the octahedral layers of atoms appear in an intermediate position as IV, V, VI and VII respectively.

4. DYNAMICAL THEORY: FIRST APPROXIMATION

The normal modes of atomic vibration in a crystal remain unaltered when a unit translation is given to the structure along any one of its three axes. Accordingly, it is sufficient to write down and solve the equations of motion of the atoms contained in any one unit cell of the structure. The features of the vibration deduced therefrom would equally well describe the possible atomic movements in the other cells of the structure. In the present problem, therefore, we have only to frame the equations of motion of a magnesium atom and of an adjoining oxygen atom in the structure

for each of the possible modes of vibration deduced from the geometry of the structure. Their solution would give us the frequencies of those modes of vibration.

The forces acting on an atom which determine its movements are those arising from the displacements of other atoms in the crystal by reason of their mutual interactions. We shall proceed on the assumption that the interactions between any two atoms are determined by their *relative* displacements measured from the positions they occupy when at rest in the crystal. The forces of interaction may be expected to be greatest as between atoms which are near neighbours and to diminish rapidly in respect of those atoms which are further and further removed from each other.

The nearest neighbours of each magnesium atom in the MgO structure are six oxygen atoms. These are situated in pairs, one on either side along the x, y and z axes of the structure. Likewise, each oxygen atom has six magnesium atoms as its nearest neighbours arranged in a similar fashion. We shall, in the first instance, proceed to work out the dynamics of the vibrations taking into account only the interactions between each magnesium atom and its six neighbouring oxygen atoms and *vice versa*. It is clear that two force-constants which we shall denote as α and β respectively would suffice to specify these interactions. The constant α refers to the interaction between an Mg atom and an O atom arising from their relative displacement *along* the direction of the cubic axis on which they both lie. The force resulting from such displacement would be parallel to the direction of the displacement. The constant β refers to the interaction arising from a relative displacement *transverse* to the line joining the two atoms and parallel to one of the other two cubic axes. In this case as well, the resulting force would be parallel to the direction of such displacement.

We denote by m_1 and m_2 the masses of the Mg and O atoms respectively. ξ_1, η_1, ζ_1 and ξ_2, η_2, ζ_2 are the displacements of the Mg and O atoms under consideration respectively along the x, y and z axes. The forces acting on these atoms are found by multiplying the displacements of the interacting atoms relatively to each of them by the appropriate force-constants and adding them up. The equations are then solved by writing

$$\xi_1 = x_1 \sin \omega t, \quad \eta_1 = y_1 \sin \omega t, \quad \text{etc.}$$

and eliminating the quantities x_1, y_1, etc., which represent amplitudes. An expression is then obtained which gives ω^2 in terms of α, β and the masses m_1 and m_2. We shall consider in turn the different modes of vibration indicated by Table I as possible for a face-centred cubic lattice,

TABLE II

Sl. No.	Description of Mode	Degeneracy
I	Oscillation of the Mg and O atoms in opposite phases ..	3
II	Tangential oscillations of the cubic planes, Mg and O atoms having opposite phases	6
III	Normal oscillations of the cubic planes, Mg and O atoms having same phases	3
IV	Normal oscillations of the octahedral planes of O atoms	4
V	Tangential oscillations of the octahedral planes of O atoms	8
VI	Normal oscillations of the octahedral planes of Mg atoms	4
VII	Tangential oscillations of the octahedral planes of Mg atoms	8
VIII	Normal oscillations of the cubic planes, Mg and O atoms having opposite phases	3
IX	Tangential oscillations of the cubic planes, Mg and O atoms having same phases	6
X	Translations	3
	Total degrees of freedom	48

and O atoms are different appear at the bottom of the table as VIII and IX respectively. The oscillations of the octahedral layers of atoms appear in an intermediate position as IV, V, VI and VII respectively.

4. DYNAMICAL THEORY: FIRST APPROXIMATION

The normal modes of atomic vibration in a crystal remain unaltered when a unit translation is given to the structure along any one of its three axes. Accordingly, it is sufficient to write down and solve the equations of motion of the atoms contained in any one unit cell of the structure. The features of the vibration deduced therefrom would equally well describe the possible atomic movements in the other cells of the structure. In the present problem, therefore, we have only to frame the equations of motion of a magnesium atom and of an adjoining oxygen atom in the structure

for each of the possible modes of vibration deduced from the geometry of the structure. Their solution would give us the frequencies of those modes of vibration.

The forces acting on an atom which determine its movements are those arising from the displacements of other atoms in the crystal by reason of their mutual interactions. We shall proceed on the assumption that the interactions between any two atoms are determined by their *relative* displacements measured from the positions they occupy when at rest in the crystal. The forces of interaction may be expected to be greatest as between atoms which are near neighbours and to diminish rapidly in respect of those atoms which are further and further removed from each other.

The nearest neighbours of each magnesium atom in the MgO structure are six oxygen atoms. These are situated in pairs, one on either side along the x, y and z axes of the structure. Likewise, each oxygen atom has six magnesium atoms as its nearest neighbours arranged in a similar fashion. We shall, in the first instance, proceed to work out the dynamics of the vibrations taking into account only the interactions between each magnesium atom and its six neighbouring oxygen atoms and *vice versa*. It is clear that two force-constants which we shall denote as α and β respectively would suffice to specify these interactions. The constant α refers to the interaction between an Mg atom and an O atom arising from their relative displacement *along* the direction of the cubic axis on which they both lie. The force resulting from such displacement would be parallel to the direction of the displacement. The constant β refers to the interaction arising from a relative displacement *transverse* to the line joining the two atoms and parallel to one of the other two cubic axes. In this case as well, the resulting force would be parallel to the direction of such displacement.

We denote by m_1 and m_2 the masses of the Mg and O atoms respectively. ξ_1, η_1, ζ_1 and ξ_2, η_2, ζ_2 are the displacements of the Mg and O atoms under consideration respectively along the x, y and z axes. The forces acting on these atoms are found by multiplying the displacements of the interacting atoms relatively to each of them by the appropriate force-constants and adding them up. The equations are then solved by writing

$$\xi_1 = x_1 \sin \omega t, \quad \eta_1 = y_1 \sin \omega t, \quad \text{etc.}$$

and eliminating the quantities x_1, y_1, etc., which represent amplitudes. An expression is then obtained which gives ω^2 in terms of α, β and the masses m_1 and m_2. We shall consider in turn the different modes of vibration indicated by Table I as possible for a face-centred cubic lattice.

The first case we shall consider is that in which the Mg atoms and O atoms oscillate as groups along the x-axis. The equations of motion are then

$$m_1 \frac{d^2\xi_1}{dt^2} = -K_0(\xi_1 - \xi_2)$$

$$m_2 \frac{d^2\xi_2}{dt^2} = -K_0(\xi_2 - \xi_1)$$

where K_0 is an abbreviation for $(2\alpha + 4\beta)$. Proceeding as already indicated, we obtain a quadratic equation for ω_1^2, the solutions of which are

$$\omega_1^2 = \frac{K_0}{\mu}, \quad \omega_{10}^2 = 0 \tag{1}$$

where μ is the reduced mass given by the formula $1/\mu = 1/m_1 + 1/m_2$. The first solution represents mode I in Table II above, while the zero frequency represents the translations appearing at the foot of that table.

The next case is that of the tangential oscillation of the cubic layers of atoms which are parallel to the yz plane along the y-axis. The alternate layers oscillate in opposite phases. The equations of motion are:

$$m_1 \frac{d^2\eta_1}{dt^2} = -K_0\eta_1 + 2\alpha\eta_2$$

$$m_2 \frac{d^2\eta_2}{dt^2} = 2\alpha\eta_1 - K_0\eta_2.$$

The solutions of these equations are:

$$\omega^2_{2,0} = \frac{\frac{1}{2}K_0}{\mu} \pm \left[\frac{K_0^2}{4\mu^2} - \frac{(K_0^2 - 4\alpha^2)}{m_1 m_2}\right]^{\frac{1}{2}}. \tag{2}$$

The alternative signs appearing in formula (2) give the frequencies of vibration ω_2 and ω_0 respectively. The higher frequency ω_2 refers to the case in which the Mg and O atoms appearing in the same yz planes move in opposite phases. The lower frequency ω_0 represents the case in which the Mg and O atoms appearing in the same yz planes move in the same phase. ω_2 and ω_0 refer respectively to the modes listed as II and IX in Table II. From formula (2) it is evident that

$$\omega_0^2 = \omega_1^2 - \omega_2^2.$$

The third case we shall consider is that in which the cubic layers of atoms in the crystal lying in the yz planes oscillate normally to themselves along the x axis, the alternate layers being in opposite phases. The equations of motion are:

$$m_1 \frac{d^2\xi_1}{dt^2} = -K_0\xi_1 - (K_0 - 8\beta)\,\xi_2$$

$$m_2 \frac{d^2\xi_2}{dt^2} = -(K_0 - 8\beta)\,\xi_1 - K_0\xi_2.$$

The solutions of these equations are:

$$\omega^2_{3,8} = \frac{\frac{1}{2}K_0}{\mu} \pm \left[\frac{\frac{1}{2}K_0^2}{\mu^2} - \frac{32\alpha\beta}{m_1 m_2}\right]^{\frac{1}{2}}. \qquad (3)$$

The alternative signs appearing in the formula give the two frequencies of vibration ω_3 and ω_8. The higher frequency ω_3 represents the case in which the Mg and O atoms which appear in any *yz* plane oscillate in the same phase, while the Mg and O atoms adjacent to each other in adjoining *yz* layers vibrate in opposite phases. The lower frequency ω_8 refers to the case in which the Mg and O atoms which appear in the same *yz* planes move in opposite phases, while the Mg and O atoms which are nearest to each other in adjacent *yz* layers oscillate in the same phase. ω_3 and ω_8 refer respectively to the modes listed as III and VIII respectively in Table II. From the formula (3), it is evident that

$$\omega_8^2 = \omega_1^2 - \omega_3^2.$$

We have next to consider the oscillations of the octahedral layers of atoms normally or tangentially to themselves. The Mg and O atoms are located in separate octahedral layers which alternate and are equidistant from each other. Hence, when two layers of Mg atoms oscillate in opposite phases, the layer of oxygen atoms midway between them remains at rest, and *vice versa*. A single equation of motion determines the frequency of oscillation for the magnesium atoms, while another such equation yields the frequency for the oxygen atoms. It is also evident that when the interactions only with the nearest neighbours are considered, the frequency for oscillations normal and tangential to the octahedral planes would not be different. We obtain

$$\omega^2_{4,5} = \frac{K_0}{m_2} \qquad (4)$$

for the modes listed as IV and V in Table II and

$$\omega^2_{6,7} = \frac{K_0}{m_1} \qquad (5)$$

for the modes listed as VI and VII in Table II,

5. DYNAMICAL THEORY: SECOND APPROXIMATION

In the foregoing, we took into account only the interactions between the atoms which are nearest to each other. This enables a first approximation to be obtained in a simple manner for the frequencies of vibration and permits of their being arranged, at least provisionally, in an ordered sequence. There is no difficulty, however, in taking the interactions with more distant neighbours into account and finding more exact formulæ. Besides the six neighbouring oxygen atoms, each magnesium atom has twelve magnesium atoms as next nearest neighbours located on the face-diagonals. It has also eight oxygen atoms as more distant neighbours located on the body-diagonals. Likewise, each oxygen atom has twelve oxygen atoms as next nearest neighbours and eight magnesium atoms as more distant neighbours. The movements of these neighbours relatively to the atom under consideration and the interactions arising therefrom have to be taken into consideration, in framing its equations of motion and deducing therefrom the frequencies of its vibration. We shall consider in succession the various modes of vibration listed in Table II.

Mode I.—In addition to the force-constants α and β already introduced, we have to consider a third force-constant γ, which expresses the interactions between the magnesium atoms and the oxygen atoms located along the body-diagonals of the cubic structure. It is readily shown that the frequencies are given by

$$\omega_1^2 = \frac{K}{\mu} \quad \text{or} \quad \omega_{10} = 0 \tag{6}$$

where K is an abbreviation for $(2\alpha + 4\beta + 8\gamma)$.

Modes II and IX.—In these modes, we have now to consider also the interactions of each Mg atom with the twelve Mg atoms in its neighbourhood. Likewise, we have to take into account the interaction of each O atom with its twelve neighbouring O atoms. The forces and displacements with which we are concerned in these interactions are parallel to each other and to one or another of the three cubic axes. Four of the atoms are located in each of the three cubic planes containing the atom under consideration. It emerges that in four cases out of the twelve, the force and the displacement are both perpendicular to the cubic plane in which the interacting atoms are situated, while in the remaining eight cases, they are both parallel to that plane. We have accordingly to introduce two new force-constants θ_1 and ϕ_1 for the interactions between the magnesium atoms, and likewise

two other force-constants θ_2 and ϕ_2 for the interactions between the oxygen atoms. The equations of motion then take the form

$$m_1 \frac{d^2\eta_1}{dt^2} = -(K + 8\theta_1 + 8\phi_1)\,\eta_1 + (K - 4\beta - 16\gamma)\,\eta_2$$

$$m_2 \frac{d^2\eta_2}{dt^2} = (K - 4\beta - 16\gamma)\,\eta_1 - (K + 8\theta_2 + 8\phi_2)\,\eta_2.$$

Substituting

$$\eta_1 = y_1 \sin \omega t \quad \text{and} \quad \eta_2 = y_2 \sin \omega t$$

and eliminating y_1 and y_2, we obtain a quadratic equation which enables $\omega^2_{3,9}$ to be expressed in terms of the force-constants and the masses m_1 and m_2.

Modes III and VIII.—Only five out of the seven force-constants already introduced appear in the equations of these two modes.

$$m_1 \frac{d^2\xi_1}{dt^2} = -(K + 16\phi_1)\,\xi_1 - (K - 8\beta)\,\xi_2$$

$$m_2 \frac{d^2\xi_2}{dt^2} - (K - 8\beta)\,\xi_1 - (K + 16\phi_2)\xi_2.$$

Substituting

$$\xi_1 = x_1 \sin \omega t \quad \text{and} \quad \xi_2 = x_2 \sin \omega t$$

and eliminating x_1 and x_2, we obtain a quadratic equation which gives $\omega^2_{3,8}$ in terms of the force-constants and the masses m_1 and m_2.

Modes IV, V, VI and VII.—We have now to introduce two additional force-constants ψ_1 and ψ_2, which represent interactions in which the force and the displacement are mutually perpendicular, the displacement being along one cubic axis and the force along another cubic axis, while the interacting atoms lie in the plane defined by the two axes. ψ_1 refers to the case in which the interacting atoms are both of magnesium, while ψ_2 refers to the case in which they are both oxygen atoms. These force-constants appear in considering the movements of the octahedral layers either normally or tangentially to themselves, by reason of the simultaneous movements along all the three cubic axes or along two cubic axes which need to be taken into account of in these cases. The equations of motion for normal and tangential movements of a magnesium atom respectively are:

$$m_1 \frac{d^2\xi_1}{dt^2} = -(K + 4\theta_1 + 8\phi_1 + 8\psi_1)\,\xi_1$$

$$m_1 \frac{d^2\xi_1}{dt^2} = -(K + 4\theta_1 + 8\phi_1 - 4\psi_1)\,\xi_1.$$

The frequencies are therefore respectively:

$$\omega_6^2 = \frac{(K + 4\theta_1 + 8\phi_1 + 8\psi_1)}{m_1}$$

$$\omega_7^2 = \frac{(K + 4\theta_1 + 8\phi_1 - 4\psi_1)}{m_1}. \qquad (7)$$

The equations of motion for normal and tangential oscillations of an oxygen atom are respectively

$$m_2 \frac{d^2\xi_2}{dt^2} = -(K + 4\theta_2 + 8\phi_2 + 8\psi_2)\,\xi_2$$

$$m_2 \frac{d^2\xi_2}{dt^2} = -(K + 4\theta_2 + 8\phi_2 - 4\psi_2)\,\xi_2.$$

The frequencies are therefore respectively

$$\omega_4^2 = \frac{(K + 4\theta_2 + 8\phi_2 + 8\psi_2)}{m_2}$$

$$\omega_5^2 = \frac{(K + 4\theta_2 + 8\phi_2 - 4\psi_2)}{m_2}. \qquad (8)$$

6. SUMMARY

The fundamental property of a normal vibration indicated by the classical dynamics, *viz.*, that the particles in the system oscillate with the same frequency and in the same or opposite phases, considered in relation to the three-dimensionally periodic structure of a crystal enables the possible modes of atomic vibration in a crystal to be uniquely characterised and enumerated. The simplicity and high symmetry of the structure of MgO enables this procedure to be carried further and the modes of normal vibration to be completely described and explicit formulæ obtained from their frequencies. It emerges that the structure of MgO has nine distinct frequencies of vibration. Expressions have been derived for these frequencies of these modes, both in the first and in the second approximation.

THE VIBRATIONS OF THE MgO CRYSTAL STRUCTURE AND ITS INFRA-RED ABSORPTION SPECTRUM

Part III. Comparison of Theory and Experiment

By Sir C. V. Raman

(*Memoir No. 127 of the Raman Research Institute, Bangalore-6*)

Received September 15, 1961

1. Introduction

Part I of this memoir dealt with the observed infra-red behaviour of MgO over the spectral range covered by the instruments at the disposal of the author. In Part II, the normal modes of vibration of the atomic nuclei in the crystal about their positions of equilibrium were deduced from the principles of classical mechanics and expressions were given for the frequencies of the nine modes which were shown to be possible. In the present part, we shall concern ourself with a comparison of the results of experiment and the consequences of the theory. Such a comparison has necessarily to be based on the nature of the relationship between infra-red activity and the modes of vibration of the atomic nuclei. We shall freely make use of the ideas and principles which have emerged from studies on the infra-red behaviour of diatomic, triatomic and polyatomic molecules, as also of crystals having more complex structures. It will be found that these ideas and principles when applied to the particular circumstances of the case enable a highly satisfactory concordance to be established between the facts of experiment recorded in Part I of the memoir and the dynamical theory developed in Part II.

2. Infra-Red Activity of the First Order

A fact which emerges very clearly from the experimental studies described in Part I is that the normal mode which is strongly active as a fundamental has also the highest frequency of all the active normal modes. The theoretical formulæ for the frequencies obtained and set out in Part II also show that the mode of vibration in which the Mg and the O atoms oscillate in opposite phases and in which the oscillation repeats itself from cell to cell without change of phase has a higher frequency than all the other eight

modes. This is obvious from the approximate formulæ given in Section 4 of Part II and the situation is not altered when the higher approximations set out in Section 5 are considered. It is further evident that this normal mode would exhibit a powerful infra-red activity of the first order. For, the displacements of electric charge resulting from the approach to or recession from each other of the two dissimilar atoms Mg and O would occur in the same phase in the successive cells of the structure and hence their effects would be cumulative.

Considering now the eight other normal modes, they can all be described as movements of the Mg atoms or of the O atoms alone or of both sets of atoms together in one or another of the different directions permitted by the symmetry of the structure. But a common feature of all the eight modes is that these movements alternate in phase along one or two or all three of the directions which are the edges of the unit rhombohedral cell of the lattice. Hence, the displacements of charge in the successive cells of the structure are in alternate phases. Therefore, when summed up over an element of volume including a block of eight contiguous cells in the structure, the displacements of charge would cancel out. It follows that all the eight modes under reference would fail to exhibit any infra-red activity of the first order. In other words, we cannot expect their fundamental frequencies to manifest themselves as absorption maxima in the spectrographic records. This again is in agreement with what is actually observed.

Here a distinction must be drawn between the four normal modes which involve simultaneous movements of the Mg and O atoms in directions which are either normal or tangential to the cubic planes of the crystal and the four other normal modes in which the Mg atoms alone or the O atoms alone oscillate in directions which are normal or tangential to the octahedral planes of the crystal. As has already been remarked in Part II, the Mg atoms and the O atoms appear in distinct layers in the octahedral planes in such manner that each Mg layer has O layers on either side of it at the same distance and each O layer has likewise Mg layers situated symmetrically on either side. Further, in the normal modes of these four species, the Mg layers on either sides of the O layers, or the O layers on either side of the Mg layer oscillate in opposite phases. As a consequence, the displacements of electric charge on either side of the middle layer are in opposite directions. When summed up over the volume element containing eight unit cells of the structure, they cancel out. Such cancellation is clearly *absolute*, in other words, it is not limited to the case in which the movements of charge are regarded as of very small amplitude and therefore strictly harmonic in character.

Thus, the two categories of normal modes, *viz.*, those in which the Mg and O atoms oscillate simultaneously and those in which they oscillate separately stand on a different footing. The former are inactive in the first-order absorption by reason of the alternation of phase in the successive cells of the structure. The absence of activity depends on the oscillation of being of small amplitude and the displacements of charge resulting therefrom being of equal magnitude but opposite in phase in successive cells. On the other hand, in the second category, the cancellation is effective irrespective of the actual amplitude of the oscillations.

3. Infra-Red Activity of Higher Orders

The considerations set forth above naturally lead us to consider the possibility of the normal modes exhibiting infra-red activity of higher orders, in other words of manifesting themselves in the absorption spectra as overtones of the fundamentals. The appearance of overtones in the infra-red absorption spectra of diatomic and polyatomic molecules is a familiar fact of experience. It is also well known that they are much weaker than the fundamentals which is indicated by the fact that their observation needs the use of much thicker absorbing layers. The explanation for their appearance usually given is based on the hypothesis of the anharmonicity of the molecular vibrations of which the effect comes into prominence when the oscillations of the atomic nuclei are of very large amplitude. In these circumstances, the periodic displacements of electric charge which give rise to the absorption of infra-red radiation include components not only of the fundamental frequencies but also the overtones of those frequencies. Absorption of the energy of radiations having the overtone frequencies and its transformation to the energy of nuclear vibrations is thereby made possible.

The important point regarding the infra-red activity of higher orders is that the amplitudes of nuclear vibration should be large. Even when this condition is satisfied, considerations regarding the symmetry of the modes of vibration may, in particular cases, totally exclude the manifestation of the effect of the periodic displacements of charge and hence also the possibility of the infra-red activity of all orders. We have already noticed such a situation in the case of the modes involving oscillation of the Mg atoms alone or of the O atoms alone in directions normal or tangential to the octahedral layers. Hence these four modes could not be expected to manifest themselves as overtones in the infra-red absorption spectra. The position is different in regard to the five other modes which involve simultaneous movements of the Mg and the O atoms. No such restriction based

on considerations of the symmetry appears in their cases. Hence we may expect overtones of all these five modes to manifest themselves in the absorption spectra, provided the necessary condition of the largeness of the amplitudes of the nuclear vibrations is satisfied.

The dynamical theory set out in Part II of the memoir is based on the well-known theorem in classical mechanics regarding the small vibrations of a connected system of particles about their positions of equilibrium. The theorem enables the relative magnitudes of the amplitudes of their vibration in any particular normal mode to be evaluated. But it leaves their absolute magnitudes undetermined. But, since we are now concerned with the absorption of radiation, the introduction of the ideas of the quantum theory which is inevitable results in making the amplitudes of vibration fully determinate. The incident radiation consists of energy quanta of magnitude $h\nu$. Assuming for the sake of simplicity that the oscillators are strictly harmonic with a frequency ν_0, their energy would go up with increasing amplitude by successive equal steps of $h\nu_0$. The successive orders of absorption would then appear as a consequence of equating $h\nu$ to $h\nu_0$, or $2h\nu_0$ or $3h\nu_0$ or $4h\nu_0$. Mechanical anharmonicity of the oscillators would only result in the energy values deviating from this regular harmonic sequence. What is needed for the possibility of infra-red activity of higher orders is that the oscillations of electric charge associated with the nuclear movements should include a harmonic series of components having the frequencies $2\nu_0$, $3\nu_0$, $4\nu_0$, etc. The energy of radiation having those frequencies can then be taken up by the moving charges and transferred to the atomic nuclei as energy of mechanical movement, in other words, as heat energy.

From what has been stated, it is clear that if we identify the mechanical oscillators in the crystal as *domains of macroscopic size*, infra-red absorptions of orders higher than the first would be impossible. For, when the oscillatory energy of such a domain is quantised, the actual amplitudes of oscillation of the atomic nuclei and therefore also the movements of electric charge associated with them would be infinitesimal. The only possibility would then be the absorption of the first order in which $h\nu = h\nu_0$ and absorptions of higher order cannot arise. Thus, for absorptions of higher order to be at all possible, we must assume the oscillators in the crystal to be of extremely small dimensions, in other words to be the unit cells of the crystal structure or small groups of such unit cells. The oscillators whose normal modes were listed and enumerated in Part II of the memoir were twice as large in each direction as the unit cells of the crystal structure. If their energies are quantised, the amplitude of the atomic oscillations in

domains of such small size would be sufficiently large to permit of infra-red absorption of higher orders than the first.

We may sum up the results of this discussion by the statement that of the nine normal modes listed in Table II of Part II of the memoir, Mode I would be active both as a fundamental and as overtones, Modes II, III, VIII and IX would be inactive as fundamentals but could be active as overtones, while Modes IV, V, VI and VII would not be active either as fundamentals or as overtones.

4. Frequencies of the Active Modes

The frequencies of the normal modes of vibration were derived in Section 4 of Part II on the assumption that the only interactions which need be taken into account are those between unlike atoms in the structure. This assumption is valid only in respect of the active mode of the highest frequency. The approximate formulæ derived on that basis are however useful as they enable the frequencies of the five active modes to be expressed in terms of each other. Two force-constants appear in the formulæ, *viz.*, α and β, α being the longitudinal and β the transverse component of the interaction between adjacent unlike atoms. It may be presumed that α is greater than β, but the ratio of α to β is not known. We assume the highest frequency of the five to be 490 cm.$^{-1}$ and compute the others for various values of the ratio α/β, *viz.*, $\alpha = \beta$, $\alpha = 2\beta$ and $\alpha = 3\beta$.

Table I below shows the results thus obtained.

Table I

Frequencies of the normal modes: Observed and calculated (*cm.*$^{-1}$)

	Mode I	Mode II	Mode III	Mode VIII	Mode IX
Observed ..	490	423	365	313	277
Calculated $\alpha = 2\beta$ ..	490	428	380	309	237
Calculated $\alpha = 3\beta$ ..	490	441	393	293	212
Calculated $\alpha = \beta$ ..	490	408	408	271	270

It will be seen that the five frequencies follow each other in the same order for all three α/β ratios, though the actual magnitudes of the calculated frequencies are different. The best agreement between the calculated and the spectroscopically determined frequencies results from the most reasonable assumption for the α/β ratio, *viz.*, that $\alpha = 2\beta$. The mode of lowest frequency, *viz.*, Mode IX is however seen to be an exception. Mode IX, it may be remarked here, is an oscillation of the cubic planes tangential to themselves, the Mg and the O atoms in those planes moving in the same phase. Like all the other modes listed in Table I except the first, it is inactive as a fundamental but active as a octave. By the nature of the case, however, such activity would be feeble. Referring to the absorption curves of the thinnest MgO film reproduced as the upper of the two records in Fig. 10 of Part I of this memoir, it will be noticed that the transmission falls off more steeply in the region of wavelengths greater than 20 μ than towards shorter wavelengths. The form of the graph between 16 μ and 20 μ indicates that a specific absorption is operative which is located midway between them, *viz.*, at about 18 μ. We are, therefore, justified in adding 277 cm.$^{-1}$ and the wavelength 36 μ to the list of normal modes and their characteristic wavelengths in the summary of experimental results which concludes Part I.

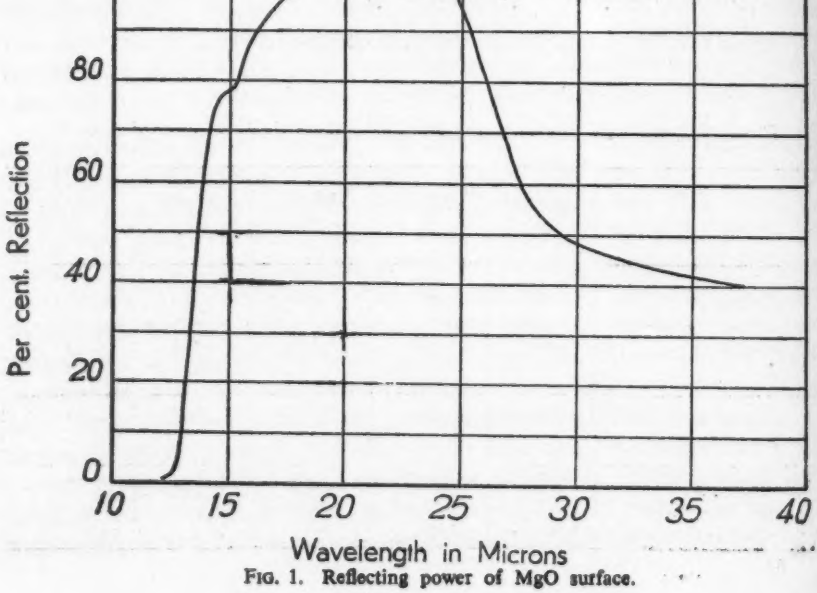

FIG. 1. Reflecting power of MgO surface.

5. Relation between Reflectivity and Infra-Red Absorpton

We may now proceed to discuss the manner in which the reflecting power of the surface of an MgO crystal changes with wavelength in the spectral range between 13 μ and 36 μ. The experimental results obtained and reported by Burstein, Oberly and Plyler (1948) have already been referred to in Part I of this memoir. Their figure which shows the reflecting power as compared with an aluminium mirror is reproduced as Fig. 1 above in the text. One might expect that the peak of the reflecting power would appear at the wavelength 20·40 μ which corresponds to the active fundamental frequency of 490 cm.$^{-1}$ However, we have also to consider in this connection, the other normal modes of vibration of the crystal. Besides the active fundamental at 20·40 μ, there is the inactive fundamental close to it in frequency which has a characteristic wavelength at 23·64 μ and a series of other inactive fundamentals at still greater wavelengths, *viz.*, 27·4 μ, 32 μ and 36 μ. Then again, in the region of wavelengths less than 20·40 μ, octaves of the normal modes appear which have their characteristic wavelengths at 10·20 μ, 11·82 μ, 13·7 μ, 16 μ and 18 μ respectively. All these octaves have been shown to be active in absorption. The possibility therefore arises of their making an observable contribution to the reflecting power of an MgO surface.

As already noticed, the absorptions located at 10·20 μ and 11·82 μ are so weak that they can only be recorded with comparatively thick plates. We may, therefore, exclude them from consideration and need only take note of the absorptions located at 13·7 μ, at 16 μ and 18 μ. It is significant that the reflective power of MgO reaches large values in this range of wavelengths. It rises very steeply at about 13·7 μ and after exhibiting an inflexion or arrest at 15 μ, goes up again in the wavelength range between 16 μ and 18 μ before it reaches the peak reflectivity beyond 20 μ. Indeed, the course of the reflectivity curve is itself the clearest demonstration that the octaves at 13·7 μ, 16 μ and 18 μ contribute notably to the reflecting power; the arrest at 15 μ arises from the frequency gap between the first two.

Figure 1 shows that the reflecting power continues to increase a little beyond 20·40 μ and is greatest at about 24 μ. Beyond 24 μ, it falls rather quickly at first and then more slowly, but remains large up to 35 μ and beyond. These facts find a natural explanation if we assume that the second fundamental having its characteristic wavelength at 23·64 μ makes a notable contribution to the reflecting power. This is indeed to be expected. For, when the frequency of the radiation is equal to or near the frequency of the active fundamental, the movements of electric charge at and near the surface

of the crystal would be large. In these circumstances, the different normal modes of vibration may be expected to influence each other in such a manner that a mode which is ordinarily inactive could be excited to activity. That the observed powerful reflection extends up to 24 μ and even beyond it is therefore not surprising.

6. FREQUENCIES OF THE INACTIVE MODES

The approximate formulæ given in Section 4 of Part II enable us also to evaluate the frequencies of the inactive modes, *viz.*, those in which the O atoms alone or the Mg atoms alone oscillate in terms of the highest active frequency, *viz.*, 490 cm.$^{-1}$ We obtain 380 cm.$^{-1}$ and 309 cm.$^{-1}$ respectively as the frequencies of vibration of the O and of the Mg atoms. It is evident, however, that these figures are an underestimate of the actual frequencies of these modes. For, as is also clear from the formulæ of Section 5 of Part II, the frequencies of these modes are determined by the interaction of each oscillating atom with six like atoms in its immediate vicinity as well as with the six unlike atoms which are its nearest neighbours. As the distance between like atoms is only $\sqrt{2}$ times the distance between unlike atoms, we may safely assume that the two sets of interactions would be of comparable magnitudes and hence that the vibration frequencies would be definitely greater than 380 cm.$^{-1}$ and 309 cm.$^{-1}$ indicated by the first approximation.

The neglect of the interactions between like atoms also results in the frequencies of oscillations of the Mg and of the O atoms normal to the octahedral planes having the same frequency as oscillations tangential to them. Actually, however, oscillations normal to the octahedral planes may be expected to have frequencies noticeably greater than the modes tangential to those planes.

Earlier, it was remarked that by reason of their geometric symmetry, Modes IV, V, VI and VII would be totally inactive, in other words, that they would be wholly inaccessible to observation by the methods of infra-red spectroscopy. This statement was, however, based on the assumption that the normal vibrations of the structure are completely independent of each other. Since, however, we are concerned with the infra-red activity of higher orders than the first, the amplitudes of vibrations involved are not small and the normal modes cannot therefore be completely independent of each other. The possibility thus arises of the inactive modes or rather of their overtones revealing themselves in the spectroscopic records by a

species of induced activity resulting from the contiguity of their frequencies to the frequencies of strongly active modes.

Referring to the spectrographic records reproduced as Figs. 3, 4, 5, 6, 7 and 8 in Part I of this memoir, it will be noticed that the transmission curve in the region between $10{\cdot}20\,\mu$ and $11{\cdot}82\,\mu$ exhibits certain curious features appearing in all of them and at precisely the same spectral wavelengths. The transmission which is a minimum at $10{\cdot}20\,\mu$ rises to a maximum and then drops to the second minimum at $11{\cdot}82\,\mu$; but between the two minima, the graph does not follow a smooth curve but bends inwards more or less sharply in the vicinity of two wavelengths, one on either side of the $11\,\mu$ ordinate. One such bend may be located at $10{\cdot}8\,\mu$ and the other at $11{\cdot}2\,\mu$. The sharp bends at these two positions appear very clearly, for example, in Fig. 6 of Part I. The frequencies in wave-numbers at which these singularities appear are respectively 925 cm.$^{-1}$ and 893 cm.$^{-1}$ If we assume that they represent the octaves of two normal modes exhibiting induced activity, their frequencies would be 463 cm.$^{-1}$ and 446 cm.$^{-1}$, substantially greater than the 380 cm.$^{-1}$ indicated by the rough calculation in which the interactions between the oxygen atoms nearest to each other are totally ignored. But the increases are not greater than what might be expected to result from such interactions being taken into account.

The induced activity of Modes VI and VII in which the magnesium atoms alone oscillate is not so conspicuously exhibited in the spectrograms reproduced in Part I of this memoir. Indications of them, however, appear in the wavelength range between $12\,\mu$ and $13\,\mu$ in Figs. 6, 7 and 8 of Part I. The sharp bends in the transmission curve at $12{\cdot}5\,\mu$ and at $12{\cdot}9\,\mu$ noticed in Fig. 8 are perhaps their clearest manifestation. Interpreting these singularities as arising from the octaves of the normal Modes VI and VII, we obtain their characteristic wavelengths at $25\,\mu$ and $25{\cdot}8\,\mu$ respectively and their characteristic frequencies as 400 cm.$^{-1}$ and 387 cm.$^{-1}$ These are substantially higher than the rough value of 309 cm.$^{-1}$ which results when we neglect the interactions between each magnesium atom and the six nearest magnesium atoms which appear in the more exact expressions for the frequencies of these modes. The observed frequencies indicate that these interactions are far from being weak or negligible. The electron atmospheres of the magnesium atoms extend further from their nuclei and hence would come into closer contact with each other in the unit cells of the structure than would be the case for the oxygen atoms. Hence the forces of interaction as between like atoms may be expected to be even more powerful for Mg than for O atoms.

7. SOME CONCLUDING REMARKS

Our purpose so far has been to show how closely the consequences of the dynamical theory set out in Part II and the observed infra-red behaviour of MgO in absorption and in reflection described in Part I fit into each other and how we are thereby enabled to obtain a clear and comprehensive view of the subject. Formal considerations based on the concept of interatomic forces, of displacements of electric charge resulting from atomic movements and of their symmetry characters were sufficient for that purpose. It would not, however, be superfluous to add a few remarks here regarding other fundamental aspects of the infra-red behaviour of crystals.

A question of some importance is the role played respectively by the atomic nuclei and by the electrons in the infra-red activity of crystals. The displacements of the massive atomic nuclei from their positions of equilibrium are necessarily involved, since the frequency of the absorbed radiation is identical with or approximates to a frequency of vibration of the atomic nuclei about their positions of equilibrium or to a small multiple thereof. But we have also to emphasise the part played by the electrons which hold the nuclei together and determine the magnitude of the interatomic forces and hence also effectively determine the frequencies of the nuclear vibrations. There can be little doubt that it is the displacement of these electrons induced by the field of the incident radiation which is the effective cause of infra-red absorption. The nuclear movements can make no direct contribution of importance to the displacements of electric charge. For, the oscillations of some of the atomic nuclei are in opposition of phase to the oscillations of the others and hence their effects would cancel out.

It follows from what has been stated above that the dynamic theory of the vibrations of the atomic nuclei and its consequences represent only one aspect of the subject of the infra-red behaviour of crystals. The other aspect is the behaviour of the electrons which hold the nuclei together in their places. These two aspects are closely related to each other. Hence, while there should be an easily observable correlation between the features of the vibration spectra of the atomic nuclei deduced from the theory and the spectral characters of the absorption and reflection of infra-red radiation as found in experiment, a complete agreement in respect of all details of their features is scarcely to be expected.

8. SUMMARY

The description of the nine normal modes of vibration and their frequency formulæ given in Part II enable them to be grouped together in

respect of infra-red activity and arranged in each group in diminishing order of frequency. A detailed comparison then becomes possible between the consequences of the theory and the experimental results set out in Part I. A comprehensive and satisfactory agreement emerges from the comparison. The modes can be identified and their frequencies determined directly from the spectroscopic records. The manner in which the reflectivity of an MgO surface varies with the wavelength of the infra-red radiation also receives a satisfactory elucidation.

THE VIBRATIONS OF THE MgO CRYSTAL STRUCTURE AND ITS INFRA-RED ABSORPTION SPECTRUM

Part IV. Evaluation of Its Specific Heat

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(*Memoir No.* 127 *of the Raman Research Institute, Bangalore-6*)

Received September 15, 1961

1. Introduction

Einstein's classic paper of 1907 introducing his theory of specific heats was based on an application of the fundamental notions of the quantum theory and of thermodynamics to the problem of determining the thermal behaviour of a body assumed to be constituted of a great number of structural elements, each of which is an oscillator having a definite frequency of vibration. Basing himself on the assumption that their energy of vibration obeys the quantum rules, Einstein obtained an expression for the total vibrational energy of the body, in other words for its heat content, in terms of the frequency or frequencies of vibration of the oscillators, their numbers and the absolute temperature. Einstein's theory and its results may be summed up by the statement that the thermal energy content of a substance is determined by the vibration spectrum of the elementary structures of which it is constituted.

A well-known theorem in classical mechanics states that the small vibrations of a system of particles result from the superposition of a set of normal modes, in each of which the particles of the system vibrate with the same frequency and in the same or opposite phases, the total number of normal modes being the same as the number of degrees of dynamic freedom of the system. The normal modes in the sense of this theorem which the structure of a crystal can exhibit may be readily deduced. The argument is the same as that used earlier in Part II of this memoir for the particular case of the MgO structure. If each unit cell of the crystal contains p atoms, the crystal has $(24p - 3)$ species of normal modes; this number is the same as the degrees of dynamic freedom of the group of $8p$ atoms included in a volume element of which the dimensions are twice as large as those of

the unit cell; the three omitted modes are the translatory movements of the group.

In the earlier parts of this memoir it has been shown that the 45 species of normal modes indicated by the general theory for MgO ($p = 2$) reduce to nine only by reason of the cubic symmetry of the crystal. These nine modes were described and their activity in the absorption and reflection of infra-red radiation was discussed. It emerged that the theory accounts in a highly satisfactory and comprehensive fashion for the observed spectroscopic properties of MgO.

TABLE I

Normal modes and frequencies

Description of the mode	Degeneracy	Frequency in cm.$^{-1}$
Oscillation of the Mg and O atoms in the unit cells in opposite phases	3	490 obs.
Normal oscillation of the O atoms in the octahedral planes	4	463 obs.
Tangential oscillation of the O atoms in the octahedral planes	8	446 obs.
Tangential oscillation of the Mg and O atoms in the cubic planes in opposite phases	6	423 obs.
Normal oscillation of the Mg atoms in the octahedral planes	4	400 obs.
Tangential oscillation of the Mg atoms in the octahedral planes	8	387 obs.
Normal oscillation of the Mg and O atoms in the cubic planes in the same phase	3	365 obs.
Normal oscillation of the Mg and O atoms in the cubic planes in opposite phases	3	313 obs.
Tangential oscillation of the Mg and O atoms in the cubic planes in the same phase	6	277 obs.
Continuous spectrum ..	3	277 $\rightarrow$0

We shall now proceed to show that the thermal energy content of the MgO crystal and its variation with temperature can be fully worked out on

the basis of the same theory as its spectroscopic behaviour. We shall make use of the original ideas of Einstein and the spectroscopic data derived from our experimental studies. The specific heat of MgO and its variation with temperature thus deduced are found to be in complete agreement with the experimental data reported in the literature. It is significant that no use whatever is made of data regarding any other properties of MgO in this connection. The power and validity of the present approach to specific heat theory are thus demonstrated.

2. THE VIBRATIONAL SPECTRUM OF MgO

Table I given above is self-explanatory. It assembles the relevant particulars set out and discussed in the preceding parts of the memoir. The total of the degeneracies listed in the second column of the table is 48, which is also the number of degrees of dynamic freedom of a group of 8 O atoms and 8 Mg atoms which forms the dynamic unit in the crystal structure. The number of such groups is one-eighth of the number of MgO "molecules" present in the crystal. This 16-atom group is the oscillator with which we are concerned in specific heat theory. 45 out of its 48 degrees of freedom are manifested as the discrete frequencies listed in the third column of the table. The remaining 3 degrees of freedom are the translations of the oscillator. They appear as the last entry of the table and are there described as a continuous spectrum with a degeneracy three and ranging in frequency from 277 cm.$^{-1}$ down to zero. The justification for these entries will appear later.

To determine the contributions to the molecular heat of the modes with discrete frequencies shown in the third column of Table I, we use the available tabulations of the Einstein specific heat function and find its value for the particular frequency at the particular temperature under consideration. *Twice the value of the Einstein function multiplied by the degeneracy of the mode and divided by* 48 *gives the contribution of the mode to the molecular heat of MgO.* Proceeding in this fashion for all the nine frequencies we can sum up the results obtained. Dividing the total obtained by 40·32 which is the molecular weight of MgO, we obtain a tabulation of the specific heat of MgO as a function of the temperature, in so far as it arises from the spectrum of vibrations with discrete frequencies.

In the general case of a crystal containing p atoms in each unit cell, the $(24p - 3)$ normal modes of vibration account for all the degrees of freedom of movement of the group of $8p$ atoms which is the oscillator in

specific heat theory except for the three degrees which represent its translations. Even in the case of the crystals with the simplest structure ($p = 1$) these translations take up only three out of every twenty-four degrees of freedom. When $p = 2$, as in the case of MgO, the translations represent only three out of forty-eight degrees of freedom. In the case of more complex crystals they form even a smaller proportion of the whole. Nevertheless, the movements within the crystal which they represent and the contributions which these make to the thermal energy cannot be ignored. We shall now proceed to consider these matters.

3. The Residual Spectrum

The translations of an atomic group within a crystal would necessarily tend to displace neighbouring atomic groups and hence would set up forces resisting the movement. We are therefore led to conclude that the degrees of freedom which do not appear as internal vibrations of our dynamic units would manifest themselves as internal vibrations in elementary volumes of larger dimensions. The larger such an element of volume is, the lower would be the limit of its possible frequencies of vibration. Hence, the translations of our atomic groups would be associated with vibrational movements in the crystal whose frequencies extend from the upper limit set by the frequencies of their internal vibration down to very low values. In other words, the vibration spectrum of MgO with its discrete set of frequencies would be supplemented by a residual spectrum which is continuous and extends down to zero frequency.

We have now to determine how the modes of vibration referred to above are distributed with respect to frequency in the residual spectrum. Low frequencies arise from internal vibrations in volume elements of large size. The number of such elements included within the crystal diminishes rapidly with increase of their linear dimensions. It follows that the density of the vibrational modes in the residual spectrum would fall off quickly as their frequency diminishes.

Consider two sets of volume elements whose linear dimensions are respectively m and n times greater than those of the atomic groups which we have recognised as the dynamic units of crystal structure. The number of such volume elements would be respectively $1/m^3$ and $1/n^3$ times smaller than the number N in the crystal of atomic groups referred to. Let ν_m and ν_n be respectively the lowest frequencies of internal vibration of these volume elements. We may reasonably assume that the vibration frequencies are inversely proportional to the linear dimensions of the oscillators. We may

accordingly write $\nu_m = f/m$ and $\nu_n = f/n$, where f is a constant having the dimensions of a frequency. In the limit when m approaches n, we may write $\nu_m - \nu_n = d\nu$. The number of oscillators whose frequencies lie within the range $d\nu$ would be thrice the difference in the number of volume elements whose lowest frequencies are respectively ν_m and ν_n, and is thus the same as $3N(1/m^3 - 1/n^3)$ in the limit where m approaches n. We may write this difference as $9N\nu^2 d\nu/f^3$. Integrating it over the whole frequency range covered by the residual spectrum, we should regain the number 3N. We are thereby enabled to identify the constant f with the upper frequency limit ν_L of the residual spectrum. The vibrational modes are thus distributed in the residual spectrum in the manner defined by the function $9N\nu^2 d\nu/\nu_L^3$.

Thus, to find the contribution to the thermal energy of the crystal arising from the residual spectrum of vibrations, we multiply the average energy of an oscillator of frequency ν as given by Einstein's theory by the number of such oscillators distributed over its range of frequency as deduced above and integrate the product between the limits ν_L and zero. The contribution to the specific heat would then be the differential of the energy thus evaluated with respect to temperature. The functions which come up for computation in this procedure are well known and as tabulations of them are available, it is a simple matter to find the contributions to the specific heat of MgO arising from the residual spectrum at various temperatures. These are then added to the contributions of the Einstein terms arising from the nine discrete frequencies of the lattice at the respective temperatures. The upper limit ν_L of the frequency range covered by the residual spectrum in this evaluation is necessarily the lowest of the nine discrete frequencies of MgO, *viz.*, 277 cm.$^{-1}$ The contribution of the residual spectrum to the specific heat at different temperatures evaluated in this manner has been entered in Tables II, III and IV below as the last entry 3D(277) after the contribution of the discrete frequencies. The latter are determined from the respective Einstein functions and are indicated in these tables as 3E(490), 4E(463), etc., etc.

4. COMPARISON WITH THE MEASURED SPECIFIC HEATS

The specific heat of MgO has been the subject of experimental determination by several investigators over different ranges of temperatures. Their data have been collected and put together in the form of a table at convenient intervals of temperature in the *International Critical Tables* (Vol. V, 1929, page 98). They are reproduced in Table V below after conversion from joules to calories.

TABLE II

Computation of specific heat

	50° K.	75° K.	100° K.	125° K.	150° K.	175° K.	200° K.	225° K.
3E(490)	0·0001	0·0049	0·0300	0·0805	0·1465	0·2163	0·2824	0·3414
4E(463)	0·0002	0·0100	0·0529	0·1315	0·2281	0·3254	0·4144	0·4921
8E(446)	0·0007	0·0255	0·1258	0·2984	0·5016	0·7003	0·8789	1·0325
6E(423)	0·0010	0·0269	0·1189	0·2643	0·4258	0·5784	0·7114	0·8240
4E(400)	0·0011	0·0252	0·0993	0·2069	0·3202	0·4228	0·5105	0·5830
8E(387)	0·0031	0·0605	0·2253	0·4525	0·6841	0·8900	1·0629	1·2049
3E(365)	0·0020	0·0310	0·1038	0·1965	0·2858	0·3625	0·4255	0·4764
3E(313)	0·0067	0·0629	0·1649	0·2715	0·3624	0·4347	0·4909	0·5342
6E(277)	0·0302	0·1993	0·4432	0·6653	0·8405	0·9729	1·0717	1·1463
3D(277)	0·1003	0·2420	0·3700	0·4647	0·5315	0·5787	0·6125	0·6372
Mol. heat	0·1454	0·6882	1·7341	3·0321	4·3265	5·4820	6·4611	7·2720
Sp. heat	0·0036	0·0171	0·0430	0·0752	0·1073	0·1360	0·1602	0·1804

A comparison of the figures appearing in Table V with the calculated specific heats at the nearest temperatures appearing in Tables II, III and IV shows that the variation of specific heat with temperature as actually measured is well represented by the theoretical computations. The excellence of the agreement is made clearer in Fig. 1 below where the theoretical curve is drawn as a continuous line while the dots represent the experimental data.

At the lowest temperature of 50° K. listed in Table II, the contribution of the residual spectrum to the specific heat forms the largest part of the whole. But as the temperature rises, its relative importance diminishes rapidly, being only 1/5th of the whole at 100° K. and 1/10th at 200° K. It thereafter diminishes progressively to its limiting value of 1/16th. These changes are a consequence of the continued increase with rising temperature of the contributions of the discrete frequencies to the specific heat, while

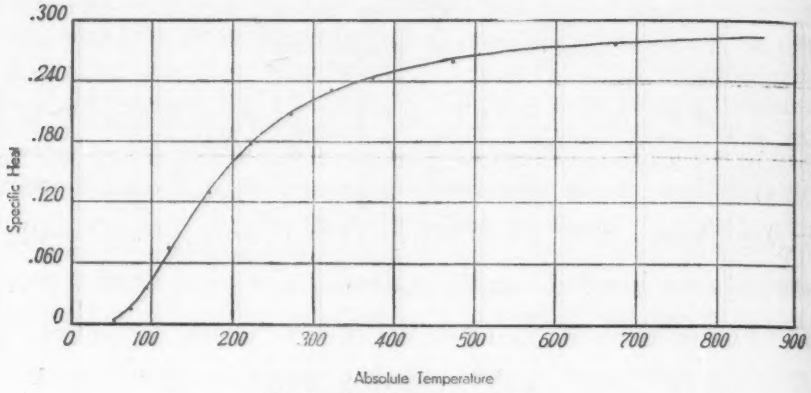

FIG. 1. Specific heat of MgO.

Calculated ———
Observed ●●●●

TABLE III

Computation of specific heat

	250° K.	275° K.	300° K.	350° K.	400° K.	450° K.	500° K.
3E (490) ..	0·3926	0·4364	0·4736	0·5321	0·5746	0·6059	0·6297
4E (463) ..	0·5586	0·6146	0·6616	0·7346	0·7870	0·8258	0·8547
8E (446) ..	1·1620	1·2708	1·3612	1·5007	1·6000	1·6731	1·7283
6E (423) ..	0·9178	0·9952	1·0591	1·1568	1·2259	1·2764	1·3122
4E (400) ..	0·6428	0·6913	0·7313	0·7916	0·8336	0·8648	0·8869
8E (387) ..	1·3205	1·4146	1·4906	1·6059	1·6867	1·7429	1·7892
3E (365) ..	0·5171	0·5500	0·5765	0·6163	0·6439	0·6627	0·6790
3E (313) ..	0·5680	0·5946	0·6161	0·6475	0·6690	0·6841	0·6949
6E (277) ..	1·2035	1·2481	1·2832	1·3340	1·3692	1·3929	1·4109
3D (277) ..	0·6558	0·6700	0·6811	0·6971	0·7079	0·7154	0·7208
Mol. heat ..	7·9387	8·4850	8·9343	9·6166	10·0978	10·4440	10·7066
Sp. heat ..	0·1969	0·2104	0·2216	0·2385	0·2504	0·2590	0·2655

TABLE IV

Computation of specific heat

	550° K.	600° K.	650° K.	700° K.	750° K.	800° K.	850° K.
3E (490)	0·6483	0·6615	0·6754	0·6835	0·6906	0·6969	0·7022
4E (463)	0·8757	0·8952	0·9088	0·9191	0·9282	0·9358	0·9423
8E (446)	1·7673	1·8054	1·8281	1·8482	1·8652	1·8799	1·8915
6E (423)	1·3440	1·3653	1·3821	1·3961	1·4079	1·4176	1·4255
4E (400)	0·9058	0·9180	0·9286	0·9371	0·9442	0·9500	0·9547
8E (387)	1·8210	1·8451	1·8649	1·8815	1·8943	1·9053	1·9141
3E (365)	0·6890	0·6975	0·7044	0·7097	0·7141	0·7176	0·7207
3E (313)	0·7033	0·7097	0·7144	0·7187	0·7221	0·7247	0·7269
6E (277)	1·4239	1·4340	1·4421	1·4486	1·4536	1·4581	1·4616
3D (277)	0·7247	0·7279	0·7303	0·7323	0·7338	0·7352	0·7362
Mol. heat	10·9030	11·0596	11·1791	11·2748	11·3540	11·4211	11·4757
Sp. heat	0·2704	0·2743	0·2773	0·2796	0·2816	0·2833	0·2846

TABLE V

Measured specific heats of MgO

Absolute temperatures ..	53°	73°	93°	123°	173°	223°
Specific heats ..	0·0033	0·0158	0·0358	0·0741	0·1290	0·1768
Absolute temperatures ..	273°	323°	373°	473°	673°	873°
Specific heat ..	0·2078	0·2317	0·2437	0·2604	0·2771	0·2915

on the other hand, the contribution of the residual spectrum soon reaches its limiting value. It will be noticed from Tables II and III that E (277) and D (277) become nearly equal to each other at temperatures higher than 250° absolute. This is a consequence of the fact that the vibrational modes

appearing in the residual spectrum are clustered near its upper limit of frequency. This is equivalent to stating that the residual spectrum arises for the most part from internal oscillations in volume elements whose dimensions are not very much larger than those of the dynamic units in the crystal. A great majority of them may be about four times as large in each direction as the unit cells of the crystal structure. Only at the very lowest temperatures, when the modes of higher frequencies cease to be excited, would any appreciable part of the thermal energy be ascribable to oscillators of still larger sizes.

5. SUMMARY

The specific heat of MgO at various temperatures from 50 to 850° absolute is computed by adding up the Einstein functions corresponding to the nine modes with discrete frequencies indicated by the dynamical theory and confirmed by infra-red spectroscopy. To this is added the contribution from a residual spectrum of vibrations of lower frequencies, the existence of which is also indicated by the dynamical theory. A very satisfactory agreement emerges over the whole range of temperatures between the calculated and observed specific heats.

THE SPECTROSCOPIC BEHAVIOUR OF ROCK-SALT AND THE EVALUATION OF ITS SPECIFIC HEAT

Part I. The Structure and Its Free Vibrations

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(*Memoir No.* 128 *of the Raman Research Institute, Bangalore-6*)

Received October 10, 1961

1. Introduction

Sodium chloride, as is well known, crystallises in the cubic system and is therefore optically isotropic. If the material is pure, the crystals are colourless and transparent over a wide range of wavelengths in the spectrum. The absorption is negligible between $0{\cdot}2\,\mu$ and $10\,\mu$, and is quite small between $10\,\mu$ and $15\,\mu$, but increases rapidly as we proceed further out into the infra-red. The technical possibility of preparing crystals of the material in large sizes from melts and of cutting out prisms from such material has made rock-salt play a highly important role in the development of infra-red spectroscopy. The range of wavelengths covered by recording instruments using NaCl prisms is from $1\,\mu$ to $15\,\mu$.

The simplicity of the composition and structure of rock-salt and the ready availability of the material make its physical properties, including especially its optical and spectroscopic behaviour, matters of very great interest from a theoretical point of view. Quite naturally, therefore, a great volume of literature exists describing the results of experimental studies and also of theoretical discussions concerning these matters. In the present memoir we are concerned with the spectroscopic behaviour of rock-salt in the region of infra-red wavelengths and its relation to the crystal structure and thermal properties of the material. It is, therefore, appropriate that we briefly recall here the major facts which have emerged from the experimental researches on the subject.

Three different methods are available for the study of the spectroscopic behaviour of rock-salt in the region of infra-red wavelengths. The first is that of determining the variation of the reflecting power of rock-salt in the region of great wavelengths. Earlier investigations indicated that the

reflecting power is quite small up to about 35 μ and that it commences to rise steeply beyond 40 μ. It exceeds 80% between 50 μ and 55 μ, and then drops to 70% at 60 μ and to 40% at 70 μ. The further diminution at still greater wavelengths is relatively more slow. The more recent investigations indicate a reflecting power greater than 90% between 50 μ and 56 μ, and also reveal additional features in the region of lower wavelengths which will be referred to later.

The second method is the study of the absorption of infra-red radiation in its passage through the material. The spectral transmission curve depends very much on the thickness of material traversed. The absorption coefficient which is small at 15 μ increases more and more steeply with increasing wavelength as we approach the region in which the reflecting power becomes large. In the latter region, the cut-off due to the reflection at the two surfaces of the plate is superposed upon the loss due to absorption. To obtain any sensible transmission in this region, very small thicknesses of the material are needed. Very interesting results were obtained and reported by Czerny (1930). Mentzel (1934) observed that the curve of percentage transmission through a rock-salt plate 24 μ thick showed an arrest between 34·5 μ and 35·5 μ, the curve running horizontally between these wavelengths though it goes down steeply with increasing wavelength both above and below this range. Barnes and Czerny (1931) found that the curve of transmission through a plate 8 μ thick likewise runs horizontally in the wavelength range between 40 μ and 44 μ. These authors also studied the transmission through evaporated films of NaCl of various thicknesses between 3·6 μ and 1·35 μ. The percentage transmission exhibited as a graph in their paper shows two downward dips located at 40 μ and 50 μ respectively, besides the highly pronounced minimum of transmission around 60 μ. The thinner films showed a further small dip in the transmission curve at about 71 μ. Mentzel in his paper listed 34 μ, 40·5 μ and 51 μ as minor maxima of absorption and 61·1 μ as the major absorption wavelength for NaCl. He also listed 33 μ, 41 μ, 42·5 μ, 47 μ and 60 μ as minor absorption peaks and 70·7 μ as the major absorption wavelength for KCl. The appearance of a whole series of minor absorption peaks is thus evidently a characteristic feature of the spectroscopic behaviour of the alkali halides.

A third and very powerful method for the study of the spectroscopic behaviour of rock-salt was initiated and employed by Rasetti (1931). The transparency of the crystal in the ultra-violet region enables the powerful 2536·5 Å radiation emitted by a water-cooled and magnet-controlled mercury arc to be used for illuminating the interior of the solid and for recording

the spectrum of the scattered radiation emerging from its interior. Rasetti made the noteworthy discovery that the spectrum thus recorded exhibits a sharp and intense line with a wave-number shift of 235 cm.$^{-1}$ from the exciting radiation. This is the most conspicuous feature observed in the spectrum which commences with a sharp rise in intensity from zero to a large value at the wave-number shift at 360 cm.$^{-1}$ and extends towards smaller frequency-shifts. The drop of intensity beyond the sharply-defined peak of the line at 235 cm.$^{-1}$ to zero in the region of smaller frequency shifts is also quite steep but is broken by the presence of a feeble band which covers the region of frequency-shifts between 220 cm.$^{-1}$ and 184 cm.$^{-1}$ The upper end of the spectrum exhibits a peak of intensity which is both smaller and not so well defined as the line at 235 cm.$^{-1}$ and covers the region of frequency-shifts between 360 cm.$^{-1}$ and 340 cm.$^{-1}$ Clearly separated from both of these principal features in the spectrum and approximately midway between them appears a group of four maxima of intensity located respectively at the frequency-shifts of 314 cm.$^{-1}$, 300 cm.$^{-1}$, 280 cm.$^{-1}$ and 258 cm.$^{-1}$ These are clearly separated from each other in the spectrum as well as in its microphotometer record.

It is proposed in this memoir to consider the spectroscopic behaviour of rock-salt in its fundamental aspects and also in relation to its activity in infra-red absorption and reflection and its activity in the scattering of light with change of frequency. A satisfactory explanation is given for the facts established by experimental study in both of these fields of research. The thermal energy content of rock-salt and the variation of its specific heat with temperature also receive a quantitatively satisfactory explanation in terms of the spectroscopic properties of the crystal.

2. The Structure of Rock-Salt

All crystals may be described as assemblages of two kinds of particles differing in their nature and properties, being respectively the heavy positively charged nuclei and the light negatively charged electrons. These two types of particles by reason of their mutual interactions hold each other in place and form a regularly arranged grouping in space. The massive nuclei are located at specific points in the structure but are capable of executing oscillatory movements about those positions. On the other hand, since the mass of the electrons is very small, they are appropriately described as forming a cloud which envelops the nuclei and fills up the volume of the solid. The attraction of a nucleus on the electrons in its immediate vicinity results in a closer association between them. As a consequence, the field due to

each positive charge is more or less completely cancelled out at a distance from it. Part of the electronic cloud however remains subject to the influence of more than one nucleus and this plays a highly important role in holding the crystal together as a coherent solid. The physical properties of the crystal and especially its spectroscopic behaviour in the lower ranges of frequency are largely determined by it.

The numbers of Na and Cl nuclei in rock-salt are equal and their dispositions in the structure are very similar. The usual description of the structure is that it consists of two interpenetrating face-centred cubic lattices, the points of which are occupied respectively by Na and Cl nuclei. Each Na nucleus appears surrounded by six Cl nuclei and each Cl nucleus by six Na nuclei, the distance between the nearest neighbours being one-half of the edge-length of the cubic cell as measured from one Na nucleus to the next or from each Cl nucleus to the next. In the atomic layers parallel to the cubic faces of the crystal, the Na and the Cl nuclei appear interspersed in such manner that each Na nucleus has four Cl nuclei as its immediate neighbours, while each Cl nucleus has four Na nuclei similarly situated with respect to it. On the other hand, in the atomic layers which are equally inclined to all the cubic axes, in other words are parallel to the faces of the octahedron, the Na nuclei and Cl nuclei do not appear together but are located in separate but equidistant layers. The distance a between neighbouring Na and Cl nuclei is also the spacing of successive atomic layers parallel to the cubic faces, while the separation of each Na layer from either of the two Cl layers adjacent to it in the octahedral planes is $a/\sqrt{3}$.

The structure of rock-salt may also be described as arising from the juxtaposition of two rhombohedral lattices displaced with respect to each other, the points of the two lattices being occupied respectively by Na and by Cl nuclei. Eight nuclei occupying the corners of a rhombohedron delineate the cells of each lattice. Six of them are located at the face-centres of a cube while the remaining two are located at opposite cube-corners.

3. THE FREE VIBRATIONS OF THE STRUCTURE

The atomic nuclei being enormously more massive than the electrons, it is permissible, when we seek to find and enumerate the normal modes of vibrations of the nuclei about their positions of equilibrium in the structure, to regard the electrons as being in the nature of massless elastic springs holding the nuclei in their places. Since the crystal also consists of an enormous number of similar and similarly situated structural units each containing its quota of atomic nuclei which is the same for all the structural units, we

may justifiably adopt the following procedure in dealing with the problem. We proceed on the basis of the theorem in the classical mechanics which states that the small vibrations of a system of connected particles about their positions of equilibrium are a summation of a set of normal modes in each of which all the particles of the system vibrate in the same or opposite phases, while the total number of normal modes is the same as the number of degrees of dynamical freedom of the system of particles. It follows that the vibrations of the atomic nuclei should satisfy the following two requirements: in any normal mode, the nuclei should all vibrate in the same or opposite phases: a normal mode should remain a normal mode following a unit translation of the crystal along any one of the three axes of the crystal structure. Taking these two principles together, it follows as a necessary consequence that following a unit translation of the crystal, the atomic nuclei in the structural unit would retain the same amplitudes of vibration while their phases would either *all* remain unaltered or else would *all* be reversed. Thus, we have two species of normal modes satisfying the requirements for each of the three axes of the structure, and since these possibilities are independent, we have $2\times2\times2$ or 8 species of normal modes in all.

We may readily apply these results to the case of a simple rhombohedral lattice at whose points only one kind of nucleus is located. Each of the 8 species of normal modes corresponds to a different disposition of the phases of vibration of the 8 nuclei situated at the corners of the cell. As each nucleus has three degrees of dynamical freedom, we have 24 available degrees of freedom. The nature of the 24 different possible movements allowed by these degrees of freedom can be readily ascertained by considering the different combinations of the phases of vibrations of the nuclei located at the points of the rhombohedral lattice. Three of them are movements of all the nuclei in the same phase, in other words, simple translations of the whole group of nuclei. Nine of them represent movements in which the nuclei lying in the same cubic plane move in the same phase while those in the adjoining cubic planes move in the opposite phase. The remaining twelve represent movements in which the nuclei lying in the same octahedral plane move in the same phase while those lying in the adjacent octahedral plane move in the opposite phase. These two groups may be further subdivided by considering the directions of movement indicated by the cubic symmetry of the whole structure. Thus the 24 possible movements may be listed as below, it being noted that the oscillations of the nuclei located in the successive planes (cubic or octahedral as the case may be) are in opposite phases.

1.	Simple translations	3
2.	Oscillations normal to the cubic planes	3
3.	Oscillations tangential to the cubic planes	6
4.	Oscillations normal to the octahedral planes	4
5.	Oscillations tangential to the octahedral planes	8
	Total ..	24

Thus, the 24 degrees of dynamical freedom of the group of 8 nuclei located at the corners of the rhombohedral cell are duly accounted for, 3 of them as simple translations and the remaining 21 as normal modes which fall into four groups with degeneracies 3, 6, 4 and 8 respectively, arising by reason of the cubic symmetry of the structure.

In the rock-salt structure we are concerned with two sets of nuclei (Na and Cl respectively) occupying the points of two similar rhombohedral lattices. Hence the foregoing description would apply to each of them. The phases of oscillation of the Na and Cl nuclei in each of the 24 modes may either be the same or opposite. Hence, we have 48 normal modes in all, corresponding to the 48 degrees of dynamic freedom of a group of 16 nuclei, 8 of Na and 8 of Cl. The three translations of each lattice separately are replaced by three translations in which the two lattices move together in the same phase, and by three oscillations respectively along the three cubic axes of the two lattices moving in opposite phases, the movement of the Na nuclei being balanced by the movement of the Cl nuclei in the contrary direction. Besides these, we have *four modes* which are coupled oscillations of the Na and Cl nuclei, two being normal and two tangential to the cubic planes with the Na and the Cl nuclei in those planes moving respectively in the same or in the opposite phases with respect to each other; also *four modes* in which the *Na nuclei alone* or the *Cl nuclei alone* present in the octahedral planes oscillate respectively normal and tangential to those planes.

4. THE NORMAL MODES OF VIBRATION

The nine normal modes of vibration and the three residual translations are listed below as a table:

		Degeneracy
I.	Oscillation of the Na and Cl lattices in opposite phases ..	3
II.	Coupled oscillations of the Na and Cl nuclei in the cubic planes:	
	(*a*) Tangential to the planes in opposite phases	6
	(*b*) Normal to the planes in the same phase	3
	(*c*) Normal to the planes in opposite phases	3
	(*d*) Tangential to the planes in the same phase	6
III.	Oscillations of the nuclei appearing in the octahedral layers	
	(*a*) Na nuclei normal to the planes	4
	(*b*) Na nuclei tangential to the planes	8
	(*c*) Cl nuclei normal to the planes	4
	(*d*) Cl nuclei tangential to the planes	8
IV.	Translations of both lattices in the same phase	3
	Total ..	48

The nine modes have been numbered and shown in the table in a particular order for reasons which will presently be explained. Figures 1, 2 and 3 in the text below illustrate the character of the oscillations in each

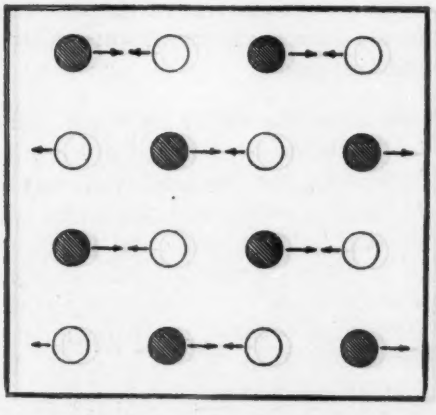


FIG. 1. Oscillation of the Na and the Cl lattices in opposite phases.

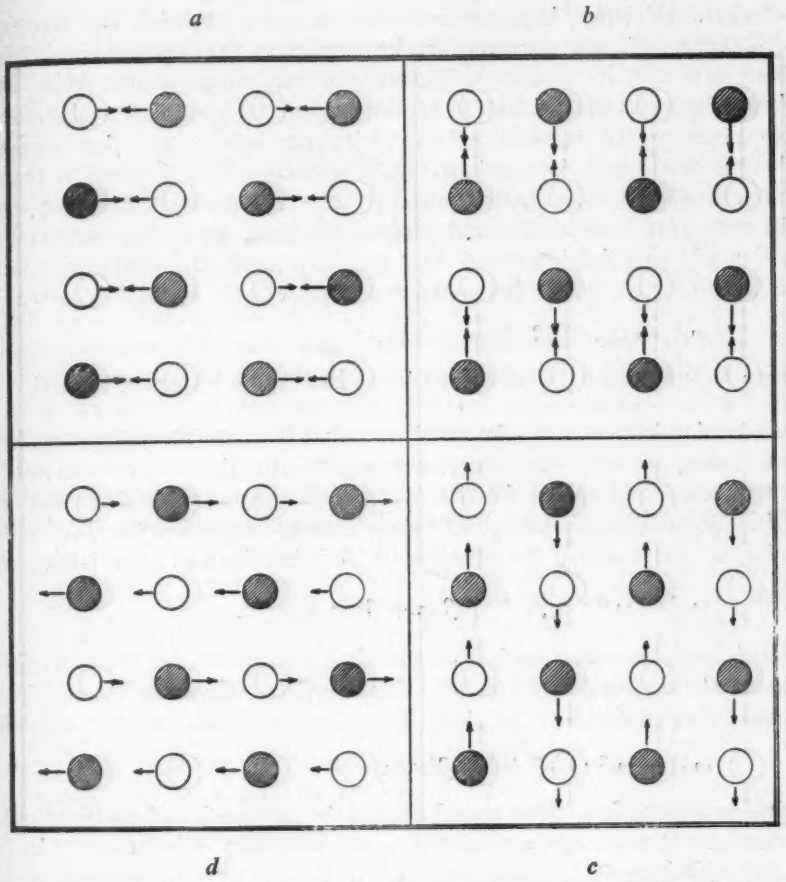
case, the numbering of the figures following the same order as in the table. The hatched circles represent the Na nuclei and the open circles the Cl nuclei. Figures 1 and 2 represent the structure viewed along a cubic axis; the cubic layers depicted are assumed to be horizontal, and the arrows represent the movements of the nuclei. Figure 3 is a view of the structure in a direction which is the intersection of an octahedral plane with a diagonal plane of the cube. It exhibits the Na and the Cl nuclei as appearing in distinct layers parallel to the faces of the octahedron.

5. THE FREQUENCIES OF THE NORMAL MODES

It would obviously be useful if the nine modes of vibration described and pictured above can be arranged in descending order of frequency, as this would greatly facilitate the comparison with the spectroscopic data and a definitive determination of their frequencies.

The mode illustrated in Fig. 1 evidently stands apart in a category by itself. This oscillation repeats itself from cell to cell, whereas in all the other eight modes the phase of vibration alternates from layer to layer. It may therefore be safely presumed that Fig. 1 represents the mode of highest frequency. The coupled oscillations of the Na and Cl nuclei in the cubic planes have been listed and pictured in the order of Figs. 2 (*a*), (*b*), (*c*) and (*d*). This would clearly also represent their arrangement in descending order of frequency. For, the movement in Fig. 2 (*a*) most closely resembles that in Fig. 1 and the movement in Fig. 2 (*b*) rather less closely, while the movements in Figs. 2 (*c*) and 2 (*d*) are clearly of a different nature. Indeed, Fig. 2 (*d*) closely resembles a transverse oscillation of the cubic layers as a whole and hence should have the lowest frequency of the four modes and indeed also of all the nine modes.

Since the masses of the Na nuclei are much smaller than of the Cl nuclei, it is evident that the modes depicted in Figs. 3 (*a*) and 3 (*b*) would both have higher frequencies than the modes shown as Figs. 3 (*c*) and 3 (*d*). The mode shown as Fig. 3 (*a*) would evidently have a higher frequency than the mode shown as Fig. 3 (*b*), since the Na layers approach each other normally in one case and move tangentially to each other in the other case. Likewise, the frequency of mode III (*c*) would be higher than that of mode III (*d*). But the differences between the normal and tangential modes in either case would not be very large for the reason that the six nearest neighbours of each oscillating nucleus are situated symmetrically around it and hence its interactions with them would be the same in both cases.



FIGS. 2 (*a*), (*b*), (*c*) and (*d*). Coupled oscillations of the Na and Cl nuclei in the cubic layers.

6. APPROXIMATE EVALUATION OF THE FREQUENCIES

We may go a little further and make a rough computation of the frequencies of all the nine modes on the basis of a simplified picture of the internuclear forces which are operative in a vibration. We notice that in Fig. 1 the movements are along a cubic axis of the crystal and represent an approach of a Na nucleus to the Cl nucleus which is its nearest neighbour on one side and a recession from the Cl nucleus on the other side. (We may interchange the Na and the Cl nuclei in this description.) The forces brought into play would be principally those resisting such approach or

recession. Of lesser importance would be those resisting the transverse displacement of each Na nucleus with respect to the four other Cl nuclei which are also its nearest neighbours on the perpendicular cubic axes. We shall assume these forces to be respectively proportional to the relative displacements, the constants of proportionality being α and β respectively. We neglect all other interactions. Such neglect is fully justified as regards interactions with more distant nuclei *of the same species*, since they move with the same amplitudes and phases. Writing down the equations of motion of two adjoining nuclei (Na and Cl respectively) and solving them, we find that the circular frequency of the vibrational mode I is given by

$$\omega_I^2 = (2\alpha + 4\beta)(1/m_1 + 1/m_2),$$

where m_1 and m_2 are respectively the masses of the Na and Cl nuclei.

Considering only the interactions between each Na nucleus and the surrounding six Cl nuclei, *and vice versa*, the equations of motion may be written down and solved for the two modes represented in Figs. 2 (*a*) and 2 (*d*). The circular frequencies of these modes may be found on evaluating the two roots of the equation which is obtained as the solution, *viz.*,

$$\omega_{II}^4 - \omega_I^2 \cdot \omega_{II}^2 + 16\beta(\alpha + \beta)/m_1 m_2 = 0.$$

Likewise, on the same basis, the equations of motion for the two modes represented by Figs. 2 (*b*) and 2 (*c*) may be written down and solved. Their circular frequencies may be found from the two roots of the equation

$$\omega_{II}^4 - \omega_I^2 \cdot \omega_{II}^2 + 32\,\alpha\beta/m_1 m_2 = 0.$$

It will be noticed from these equations that the frequencies of the two coupled oscillations in each case are related to the frequency ω_I of mode I by the simple relations

$$\omega_{II}\, a^2 + \omega_{II}\, d^2 = \omega_I^2$$

and

$$\omega_{II}\, b^2 + \omega_{II}\, c^2 = \omega_I^2.$$

It is evident also from these relations that mode I has the highest frequency of all the five modes considered. They can all be computed if the values of α and β are known. Alternatively, if the frequency of mode I is known and some reasonable assumption is made for the ratio α/β, as for example that $\alpha = 2\beta$, the frequencies of the four other coupled oscillations of the Na and Cl nuclei can be found from that of the mode of highest frequency.

Assuming that the frequency of mode I expressed in wave-numbers is 180 cm.$^{-1}$ and that $\alpha = 2\beta$, we find the following values for the frequencies of the four other modes also in wave-numbers:

Frequency of mode I (assumed)	180 cm.$^{-1}$
Frequency of mode II (*a*) (calculated)	158 cm.$^{-1}$
Frequency of mode II (*b*) (calculated)	140 cm.$^{-1}$
Frequency of mode II (*c*) (calculated)	113 cm.$^{-1}$
Frequency of mode II (*d*) (calculated)	87 cm.$^{-1}$

Thus, the descending sequence of frequency in which these five modes were arranged in the table and numbered in the figures is seen to be correct. It should be remarked however that the calculations ignored the interactions between each nucleus and the others of the same species present in the adjacent layers and moving with the same amplitude but in an opposite phase. As these nuclei are however situated further from it than the nuclei whose interactions have been considered, the calculations of frequency cannot be seriously in error. But they can only be considered only as approximations.

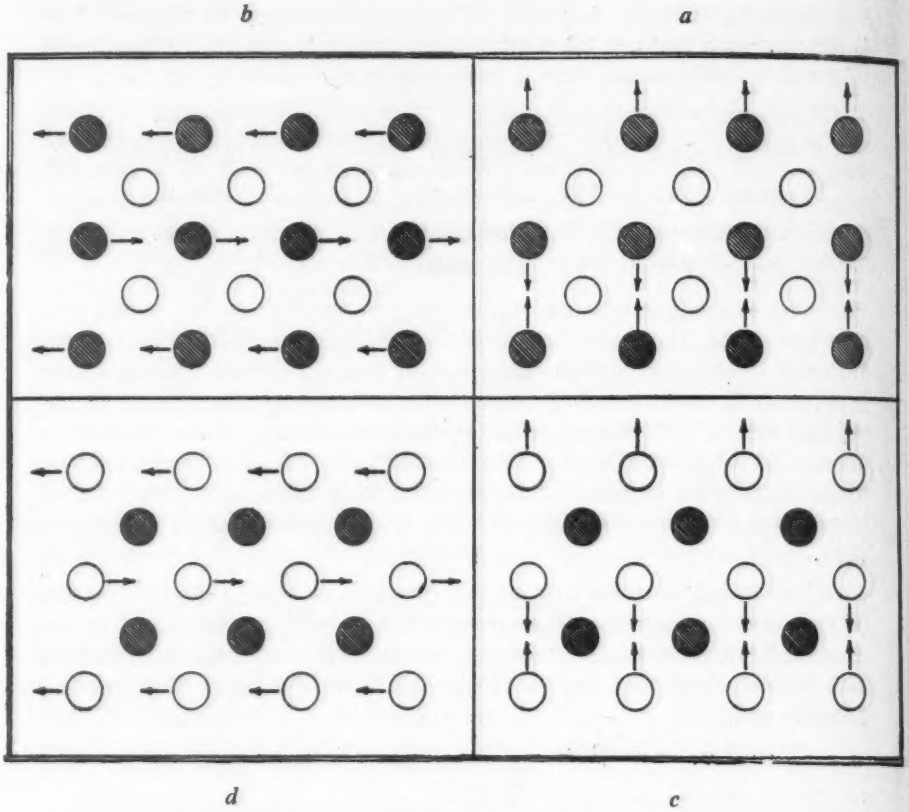
Considering now the four modes pictured as Figs. 3 (*a*), (*b*), (*c*) and (*d*) it is obvious that their frequencies would be very simply related to that of mode I, provided that we take into account only the interactions between each Na nucleus and the six Cl nuclei around it, and *vice versa*. The relevant formulæ are:

$$\omega_{III}^2 = (2\alpha + 4\beta)/m_1$$

for the modes III (*a*) and III (*b*) and

$$\omega_{III}^2 = (2\alpha + 4\beta)/m_2$$

for modes III (*c*) and III (*d*). If we take the frequency of mode I as 180 cm.$^{-1}$ in wave-numbers, that of modes III (*a*) and III (*b*) come out as 140 cm.$^{-1}$ and that of modes III (*c*) and III (*d*) as 113 cm.$^{-1}$ This procedure for deducing the frequencies results in the modes of vibration tangential and normal to the octahedral planes having the same value. This is a consequence of our having neglected the interactions between the nuclei of the same kind which are in relative movement and hence would influence the frequencies of the vibration. As will be seen from Figs. 3 (*a*), (*b*), (*c*) and (*d*), the adjacent layers of similar nuclei slide past each other in the tangential modes, while they alternately approach and recede from each other in the normal modes. The interactions between the moving layers would, in these circumstances, not be negligible. Their influence on the frequencies



FIGS. 3 (*a*), (*b*), (*c*) and (*d*). Oscillations of the Na and the Cl nuclei in the octahedral layers.

of vibration would evidently be greater in the normal modes than in the tangential ones, thereby making the frequencies in these cases different. It is also evident that the frequencies of 140 cm.$^{-1}$ and 113 cm.$^{-1}$ as computed and shown above would be slightly smaller than the correct values for the tangential modes, and definitely less than the correct values for the normal modes. Each moving nucleus comes under the influence of six nuclei of the same kind and six nuclei of the other kind in its movement, the distances between the interacting nuclei being $2a/\sqrt{3}$ and a respectively. In these circumstances, an increase of say 10% in the frequencies of the tangential modes and say 20% in the frequencies of the normal modes may be hazarded

as a rough estimate of an alteration in the calculated frequencies produced by taking the interactions between like nuclei also into account.

7. Summary

The nine normal modes of free vibration of the rock-salt structure have been deduced theoretically and fully described. They have been arranged in descending order of frequency and an approximate estimate of their frequencies is also given. The mode of highest frequency is that in which the Na and Cl lattices oscillate in opposite phases.

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THE SPECTROSCOPIC BEHAVIOUR OF ROCK-SALT AND THE EVALUATION OF ITS SPECIFIC HEAT

Part II. Its Infra-Red Activity

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(*Memoir No.* 128 *of the Raman Research Institute, Bangalore-6*)

Received October 16, 1961

1. Introduction

The basic questions in relation to the infra-red activity of crystals are, *firstly*, how does the activity arise and *secondly* how is it related to the structure of the crystal? Since these two questions are closely connected, it is evident that answers to them could most appropriately be sought for in relation to crystals of the simplest possible structure and composition and of the highest possible symmetry. For, the various complications such as those arising from the details of molecular structure, molecular anisotropy and molecular interactions would be avoided and the questions requiring answer would present themselves in the most definite and tractable form. It is also essential that the case considered is one which could be most completely explored by spectroscopic methods and experimental data obtained which could be compared with the consequences of theory. NaCl is a case in which these requirements are satisfied and hence is very suitable as a test-case.

Infra-red activity minifests itself in three different ways which are susceptible of experimental study. Firstly, we have the refractivity of the material which as we pass from the visible into the infra-red region clearly exhibits the effect of infra-red activity. Secondly, we have the reflecting power of crystal surfaces, and thirdly, the absorption of radiation in its passage through the material. The absorption is a mass-effect and where it is very powerful as in the case of rock-salt, we could scarcely expect studies of it to reveal its relationship to the spectroscopic behaviour in an obvious fashion. It is indeed necessary to obtain spectrographic records of the percentage transmission by plates whose thickness is varied step by step over the widest possible range and to make a comparative study of the records in order to obtain any useful indications.

In the present memoir, we shall cover various aspects of the subject. Firstly, we shall consider it from a purely fundamental and general standpoint. Secondly, we shall discuss the relation between infra-red activity and the free vibrations of the structure as considered in the first part of the memoir. Thirdly, the results of experimental studies of the kind indicated in the foregoing paragraph will be presented. Lastly, these experimental results will be correlated with those of Czerny and collaborators mentioned in the first part of the memoir and then compared with the consequences of theory.

2. The Origin of Infra-Red Activity

Viewed from the point of view of classical mechanics, the absorption of infra-red waves in their passage through a crystal can be considered as a transfer of energy which is effected by the electric field of the waves acting on the charged particles in its structure and setting them in vibration. If the frequency of the field is sufficiently close to the frequency of a normal mode of vibration, the possibility of resonance arises. But whether such resonance would actually occur is a question that needs examination.

As there are two types of charged particles in the structure, *viz.*, the nuclei and the electrons, it is appropriate at first to consider the effects of the radiation field on them separately. The nuclei besides being positively charged possess masses enormously large compared with those of the electrons. It is a familiar consequence of classical mechanics that in a normal vibration the common centre of inertia of the particles of the system remains at rest. Likewise, in our present problem, the common centre of inertia of all the nuclei included in the vibrating structural unit would remain at rest in any free vibration. Hence, when all the nuclei have the same mass, as for example, in a crystal of diamond or silicon or germanium, the common centre of the positive charges carried by the nuclei would remain undisturbed during the vibration. It follows that when the crystal is traversed by infra-red radiation, the forces exerted by the field on the positive charges would in the sum total be unable to transfer energy to the crystal and hence they could not possibly excite such vibrations. The situation would be the same even when the nuclei in the crystal belong to different species, provided that the ratio of the masses to the charges is the same for the different nuclei, as is the case for example with rock-salt or quartz. It follows that the positive charges of the nuclei do not play any role in the infra-red activity of the crystals. *All the observed effects arise from the action of the field of incident radiation on the negatively charged electronic clouds.*

The question then arises why the infra-red absorption spectra of a crystal should be related in any way or bear any resemblance to the spectrum of free vibrations of the atomic nuclei considered in the first part of the present memoir. The answer to this is that there is a connecting link between the infra-red absorption and the vibration spectrum of the atomic nuclei. This is to be found in the fact that the electronic clouds are held in the crystal by their interactions with the positively charged nuclei; *vice versa*, the nuclei are held in their places by their interactions with the electronic clouds. Hence, a periodic disturbance of the electronic clouds produced by the field of the radiation *may* tend to disturb the nuclei from their positions and set them in synchronous vibration. *Vice versa*, vibrations of the nuclei *may* tend to disturb the electronic clouds and set them in synchronous vibration. A periodic movement of the electronic cloud is a *sine qua non* for the production of the effects described under the term of infra-red activity. Hence, unless a free vibration of the nuclei is associated with and gives rise to such a movement of the electronic clouds, it would not be set up under the action of the periodic external electric field.

The foregoing discussions, apart from emphasising the fundamental role played by the electrons in the absorption of infra-red radiation and other related effects, make it clear why the *asymmetry* of the nuclear vibrations plays such a highly important role in infra-red activity. For, in the absence of such asymmetry, there would be no periodic displacement of the electronic clouds and hence no excitation of the nuclear vibrations.

3. INFRA-RED ACTIVITY OF THE NORMAL MODES

From what has been stated in the preceding paragraph, it is clear that the four modes in which the Na nuclei alone or the Cl nuclei alone oscillate either normally or tangentially to the octahedral planes could not exhibit any infra-red activity. For, in these modes, two layers of Na nuclei approach or recede from an intermediate layer of Cl nuclei symmetrically on either side with equal amplitudes. Hence, the movements of electronic charges resulting therefrom when summed up over each of the structural elements of the crystal would vanish. This conclusion would be valid irrespective of the actual amplitude of the nuclear movements. Hence the four modes of the octahedral class can be disregarded in our consideration of the infra-red activity of the normal modes of vibration. We need only examine the behaviour of the five other normal modes in which the Na and Cl nuclei appearing in the cubic layers execute coupled oscillations.

The principal normal mode of highest frequency in which the Na and Cl lattices oscillate in a balanced movement stands in a class by itself

and will therefore be considered first. By reason of the difference in the masses of the Na and the Cl nuclei, the amplitude of movement of the Na nuclei would be proportionately greater than that of the Cl nuclei and hence the amplitudes of oscillation of the electronic clouds respectively held by them in close association would also be different. But by reason of the difference in the positive charges of the two nuclei, the negative charge of the electrons so held would be smaller for the Na nuclei than for the Cl nuclei. The resulting displacements of negative charge when totalled up would therefore cancel out more or less completely. What would be left over and needs special consideration is the part of the electronic cloud which comes under the influence of both sets of nuclei and its movements under the action of the field of incident radiation.

During one half-period of the oscillation, the Cl nucleus on one side of a Na nucleus approaches it and the Cl nucleus on the other side recedes from it. During the other half-period, these movements are reversed. It is clear, however, that the asymmetric displacements of electric charge with which we are here concerned would be in the same direction on both sides of the Na nucleus and that they would be reversed in successive half-periods of the oscillation. Hence, they would not cancel out but would add up to produce a periodic displacement of negative charge having the same frequency as the incident waves. Further, since the oscillation of the nuclei repeats itself from cell to cell, the effects of all the cells would add up and hence would result in a large effect. In other words, the normal mode of highest frequency would be powerfully infra-red active, and it would need only a very small thickness of the material to make such activity manifest. The coherent phase relationship between the oscillations of electric charge in the adjacent cells of the structure would have a further consequence. The oscillating electric charges at and near the surface of the crystal would act as secondary sources of radiation and their conjoint action would result in a powerful reflection of the incident radiation at the surface of the crystal. This effect would be most powerful at and near the frequency of the normal mode under consideration. For, at such frequencies, the movements of the nuclei would be most vigorous and hence the displacements of negative electric charge associated therewith would be large.

The four other modes of coupled oscillation of the Na and Cl nuclei stand on an entirely different footing. In these modes, the oscillation reverses its phase as it passes from one cubic layer of the crystal to the next. Hence, the displacements of electric charge would be in opposite phases in the alternate layers and when summed up would cancel each other out. Hence, these four normal modes would not exhibit any infra-red activity.

This statement is however subject to various qualifications, since it rests on two assumptions. The first assumption is the complete independence of the normal modes of vibration. The second assumption is that the amplitudes of vibration are extremely small. If these assumptions are not valid, the conclusion drawn that the four normal modes are inactive would also need reconsideration.

4. OVERTONES OF THE NORMAL FREQUENCIES

So far, we have proceeded on the basis of the theory of small vibrations of a connected system of particles in the classical mechanics. The curious feature of the case is that the forces which are effective in exciting the vibrations are not those acting on the masses, *viz.*, the positively charged nuclei, but on the springs, *viz.*, the negatively charged electrons which hold them together and effectively determine their frequencies of vibration.

We have now, of necessity, to introduce the fundamental notions of the quantum theory. The energy of the radiation appears in quanta proportional to its frequency and if such energy is to be completely taken up by the oscillators with which we are concerned, *viz.*, the group of 8 Na and 8 Cl nuclei, the frequency of the mechanical oscillations should be the same as that of the incident radiation. In other words, we would have resonance. But we have also to consider the cases in which the frequency of the free vibration is not the same as that of the incident radiation. Of special interest are the cases in which the frequency of the incident radiation is a small multiple of the frequency of the oscillator, and hence the absorption of energy would involve the acceptance by the oscillator of two, three or larger number of quanta of the energy of radiation. It may be presumed that the probability of this happening would diminish rapidly with the increasing number of quanta thus taken up, in other words that the absorption would then become rapidly weaker and weaker in the series. But since we are dealing with a crystal, there should be no difficulty in observing such absorption. We have only to increase the thickness of the absorbing plate sufficiently to be able to record the absorption spectra of the higher orders.

The further question then arises, what is the factor which determines the diminishing strength of the absorption with the increasing number of quanta taken up by the oscillator? We may remark that an increase in the magnitude of the energy taken up involves an increase of the amplitude of the resulting vibration. The absolute dimensions of the oscillator being small, the amplitude of the movements corresponding only to one quantum of energy could by no means be considered as small, and the amplitude corresponding to two, three more quanta would far transcend any such

limits. The movements of the electronic clouds which are the operative cause of infra-red activity would become more and more nearly comparable with the dimensions of the electronic clouds more closely associated with the Na and the Cl nuclei. It would clearly, in these circumstances, cease to be justifiable to assume that the classical theory of small vibrations and its consequences would correspond with the facts of experiment. In other words, the appearance of overtones of the normal frequencies in absorption and the diminishing strength of such absorption with increasing frequency are both associated with the increasing amplitude of the resulting vibrations and the consequences arising therefrom.

We have already noticed that the normal mode of highest frequency would exhibit infra-red activity with great strength. It follows that this mode would also exhibit infra-red absorption of the higher orders in a conspicuous manner. It is also evident that the absence of infra-red activity of the four other modes of coupled oscillation which was remarked upon earlier would not extend to absorption of the higher orders corresponding to frequencies which are multiples of the frequencies of free vibration in those modes. For, their inactivity in the first order absorption was ascribed to the opposition of the phase of the oscillation in the alternate layers of the structure in those modes. When the amplitudes are large, the displacements of charge in one layer and in the next layer where the phase of the motion is opposite would not be numerically of equal magnitude and hence when they are summed up they would not cancel out completely. The residue would have twice the frequency of the oscillation. The octaves of these modes could therefore be expected to appear in absorption with considerable strength.

Another important consequence of the amplitudes of vibrations not being small is that the various normal modes would cease to be completely independent of each other. The sharpness of resonance which is a characteristic consequence of the theory of small vibrations would be notably departed from when, as in the present case, we have five normal modes which are spread over a wide range of frequencies and are not restricted to small amplitudes of vibration. In these circumstances, the energy of the incident radiation can be taken up for the excitation of vibrations which may be described as a superposition of two or more normal modes approximating to each other in frequency. It is also possible for a vibration to be excited which may be described as a superposition of one normal mode as a fundamental with another normal mode as an overtone with a frequency which is not very different. More generally, the radiation may excite vibrations which may

be described as a summation of two or more normal modes differing from each other in frequency and either as fundamentals or as overtones.

Earlier, we discussed the reflection of infra-red radiation which occurs when the incident radiation has the same frequency as the normal mode of highest frequency. We have now to remark that reflections of notable strength may also arise at other frequencies in consequence of the incident radiation exciting superposed vibrations of the kind referred to above with sufficiently large amplitudes. We shall have occasion to consider such cases later in this memoir.

5. THE ABSORPTION SPECTRA OF ROCK-SALT

Some excellent specimens of transparent salt were available in the museum of the Institute and it appeared worthwhile to study their behaviour in absorption, making use of the Leitz infra-red recording spectrophotometer with KBr optics which covers the spectral range between 13 μ and 24 μ. This, of course, is much outside the wavelength range within which powerful infra-red reflections are exhibited by rock-salt. The considerations set forth above however indicate that the absorption spectra of the higher orders could be recorded within the range of the instrument and evidence thus obtained both for the existence of such absorption and its relation to the specific modes and frequencies of vibration of the atomic nuclei in the crystal. Nine different thicknesses of the absorbing material ranging from 5·2 cm. down to 1·5 mm. were employed and their transmission percentages were recorded. A comparative study of the records reveals some very significant features. To illustrate them, the nine records are reproduced below in the text as Figs. 1 to 9, the absorption path being indicated below each figure.

Figure 1 recorded with a block 5·2 cm. thick exhibits nearly complete transparency at 13 μ, followed by a progressive fall to opacity at 18·5 μ, beyond which there is a complete cut-off of all transmission. Very similar features are also exhibited in Figs. 2 and 3 which were recorded with blocks which were respectively 4·3 and 2·8 cm. thick. It will be noticed, however, that a rapid improvement in transparency in the wavelength range between 13 μ and 14·5 μ appears as the absorption path is diminished. Whereas a difference of 18% in the transmissions at 13 μ and 14·5 μ is noticed in Fig. 1 for the block 5·2 cm. thick, the difference is only 12% in Fig. 2 for a thickness of 4·3 cm. and only 5% in Fig. 3 for a thickness of 2·8 cm. On the other hand, in the region of longer wavelengths, as will be seen on a comparison of Figs. 1, 2, 3, 4 and 5, there is little or no change in transmission produced by the large change in the absorption path from 5·2 to 1·5 cm.

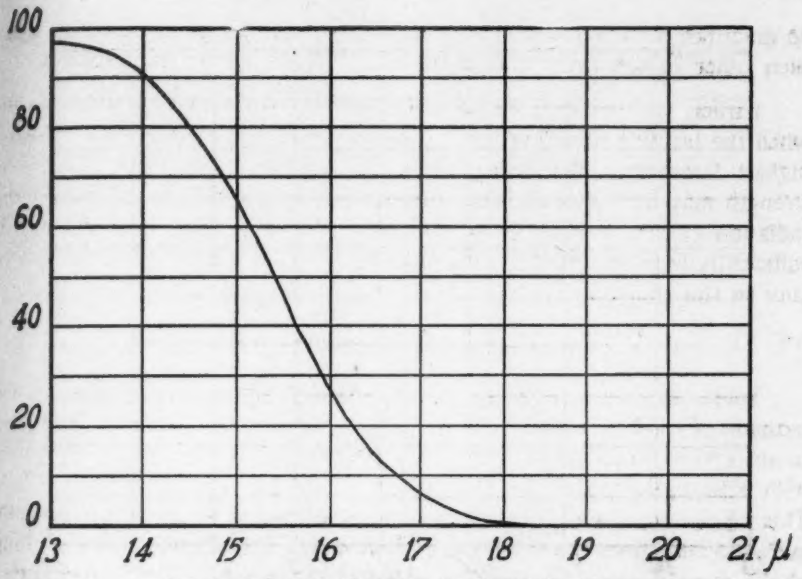

FIG. 1. Infra-Red Absorption by Rock-Salt : 5·2 cm.

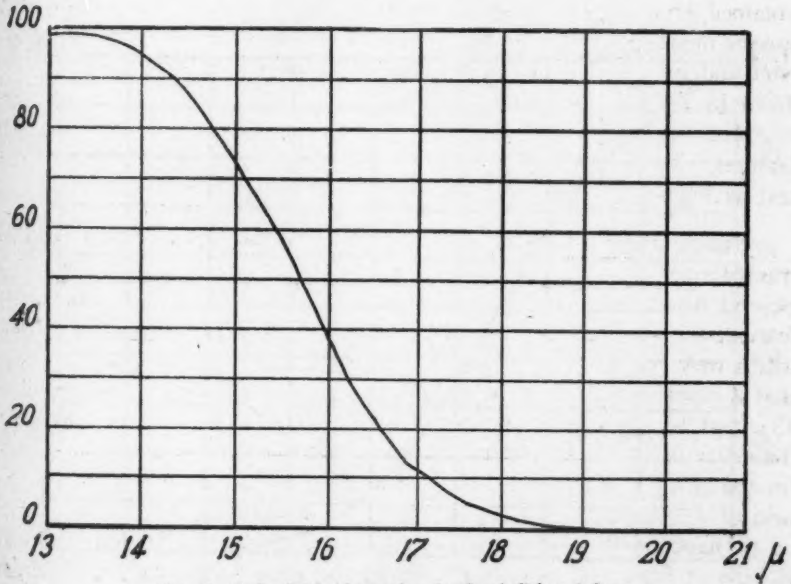

FIG. 2. Infra-Red Absorption by Rock-Salt : 4·3 cm.

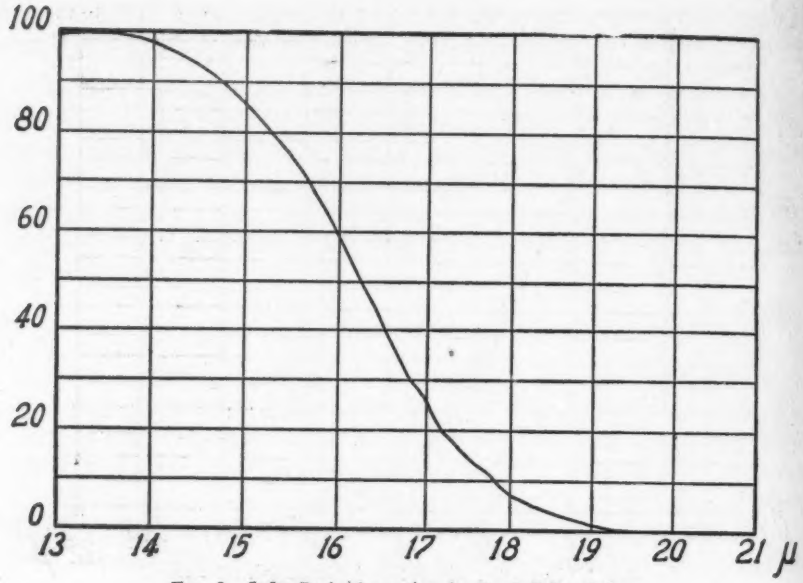

FIG. 3. Infra-Red Absorption by Rock-Salt : 2·8 cm.

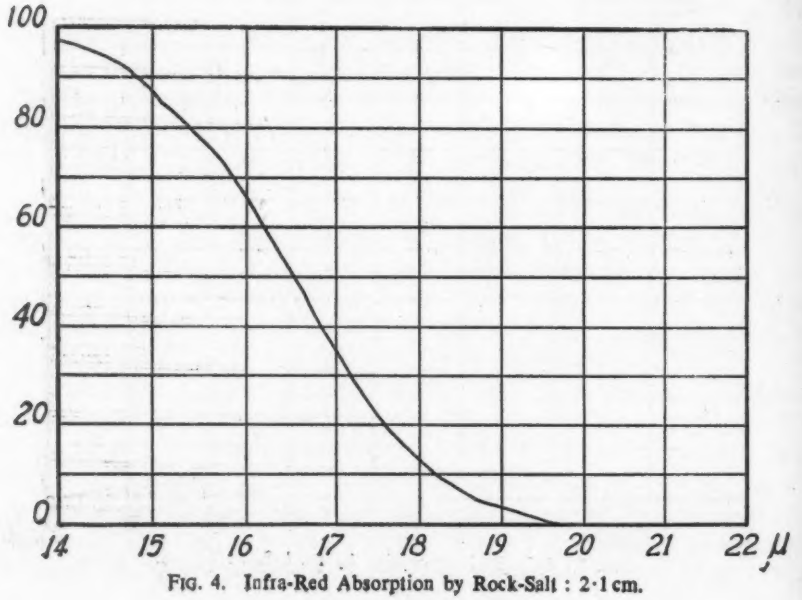

FIG. 4. Infra-Red Absorption by Rock-Salt : 2·1 cm.

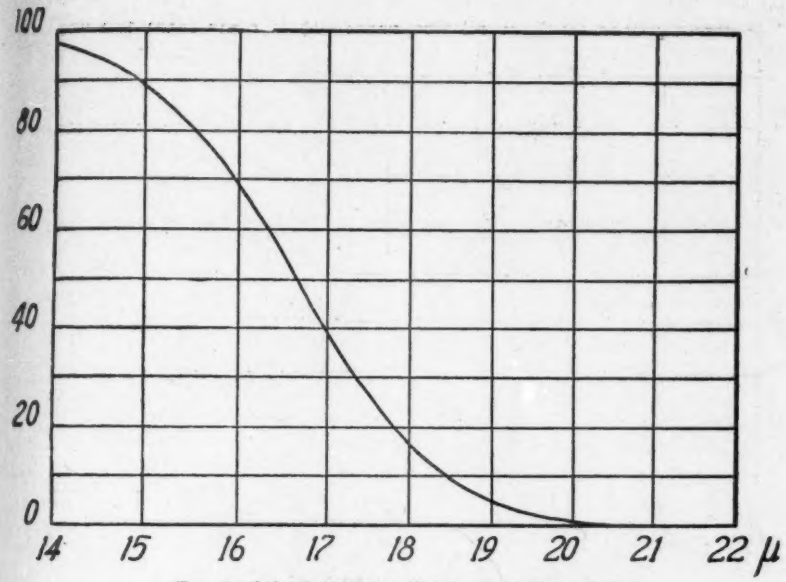

FIG. 5. Infra-Red Absorption by Rock-Salt : 1·5 cm.

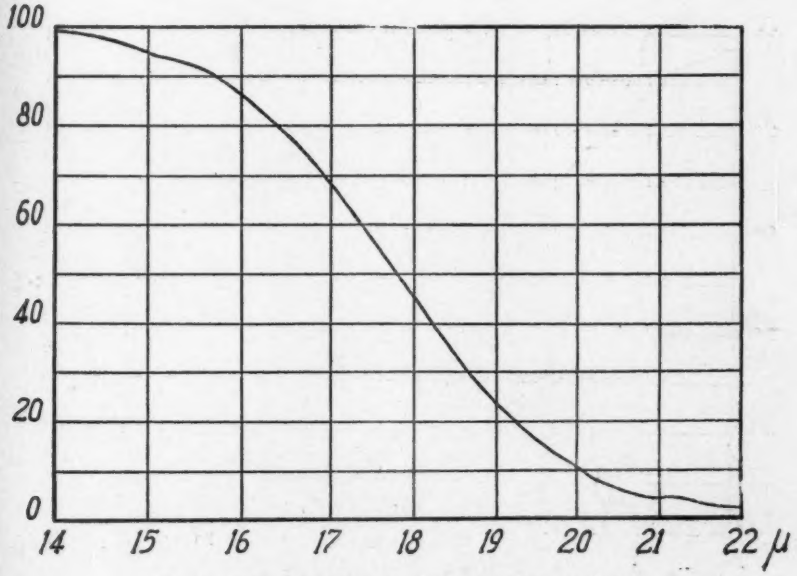

FIG. 6. Infra-Red Absorption by Rock-Salt : 0·8 cm.

The cut-off of the longer wavelengths persists and the transmission at 19 μ is either zero or very small in all five cases. It is clear from the spectrographic records that the absorptions in the spectral regions from 13 μ to 19 μ and from 19 μ to 24 μ are of totally different orders of magnitude.

As is to be expected in the circumstances stated above, very striking changes appear in the form of the transmission curve when the thickness is greatly reduced and is of the order of a few millimetres only. Figures 6 to 9 are the records respectively for plates of thickness 8 mm., 4 mm., 2·5 mm. and 1·5 mm. The cut-off in the region of the longer wavelengths has now disappeared and is replaced by a transmission which increases from 25% at 19 μ to 72% at the same wavelength as the thickness is diminished from 8 to 1·5 mm.

We may here draw attention to the remarkable fact that the percentage transmission curves are by no means always smooth graphs showing a progressive and continuous fall in transmission with increasing wavelength. Dips and sudden changes in direction are a noticeable feature. That they represent genuine features and not accidental faults in recording is shown by their appearance in the graphs for different thicknesses at the same wave-

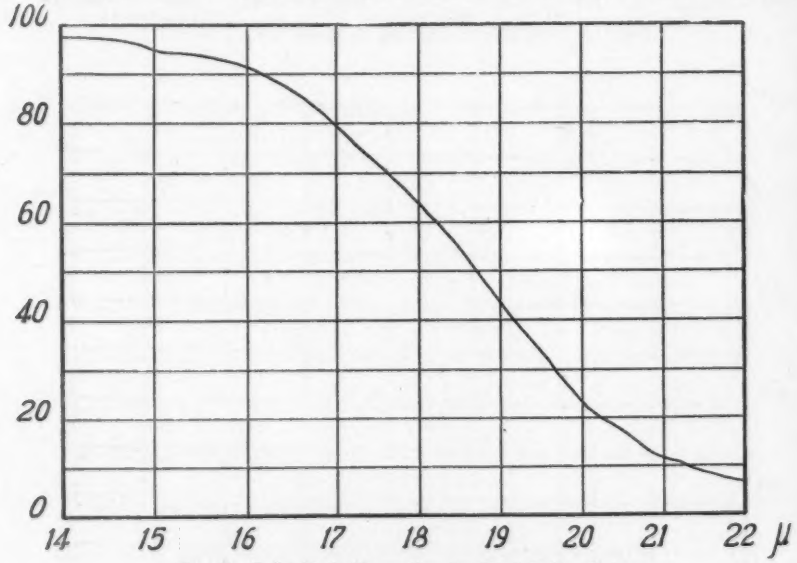

FIG. 7. Infra-Red Absorption by Rock-Salt : 0·4 cm.

lengths. It will suffice here to draw special attention to Fig. 8 which is the record for a plate 2·5 mm. thick. The curve as reproduced commences

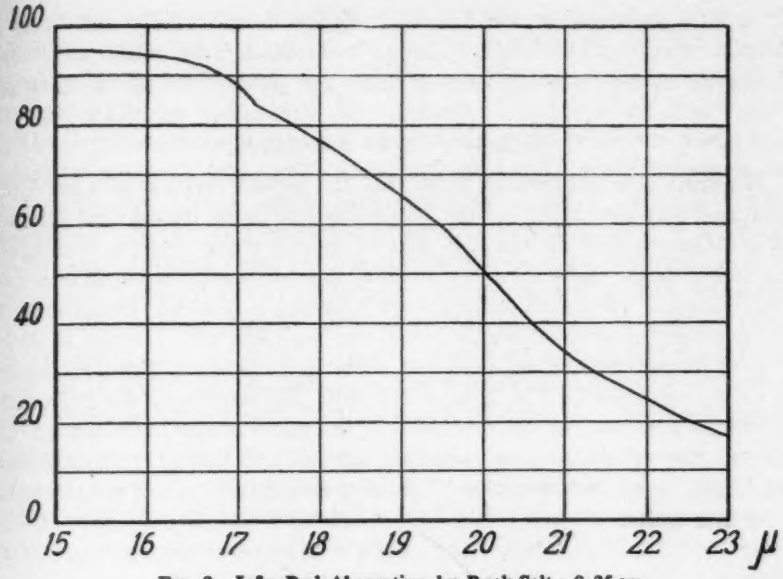

FIG. 8. Infra-Red Absorption by Rock-Salt : 0·25 cm.

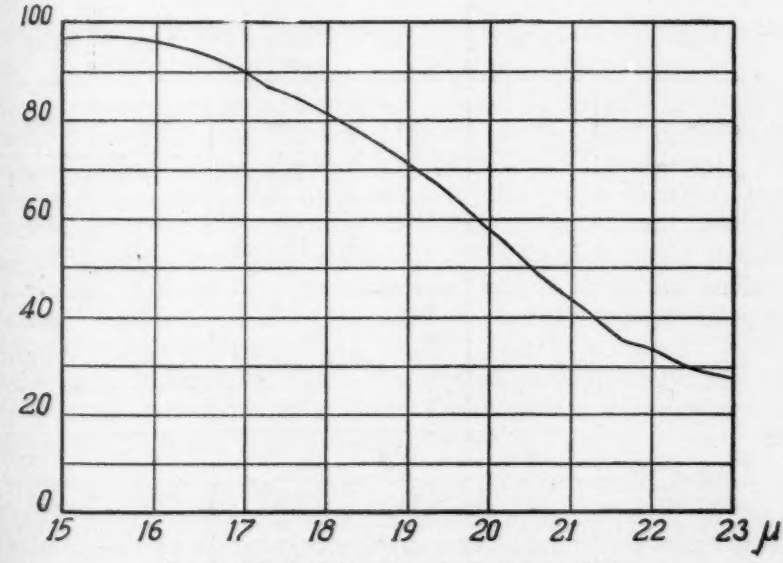

FIG. 9. Infra-Red Absorption by Rock-Salt : 0·15 cm.

with a 90% transmission at 15 μ. This drops down rapidly and takes a sudden turn at 17·2 μ. Another change in direction is noticeable at 19·5 μ, still another at 20·7 μ and finally a small but distinct change in direction at 22 μ.

6. SIGNIFICANCE OF THE RESULTS

We shall now proceed to show that the experimental results set forth above and also the results of the published studies of Barnes and Czerny, and of Mentzel cited in the first part of this memoir find an intelligible explanation in the light of the theoretical considerations expounded earlier in this memoir. We shall commence by assuming that the frequencies of the five modes of coupled oscillation of the Na and the Cl nuclei in rock-salt at room temperature are as shown below in Table I, both as wavelengths and as wave-numbers. The figures find their justification in the theoretical calculations presented in the first part of the memoir and corrected on the basis of the spectrographic data emerging from Rasetti's investigation. Table I also shows the overtones of the five frequencies up to and inclusive of the fifth order.

TABLE I

Vibration frequencies of rock-salt

Mode		I Order	II Order	III Order	IV Order	V Order
I	cm.$^{-1}$ ..	180	360	540	720	900
	μ	55·6	27·8	18·5	13·9	11·1
II (*a*)	cm.$^{-1}$ ..	150	300	450	600	750
	μ	66·7	33·3	22·2	16·7	13.3
II (*b*)	cm.$^{-1}$ ..	129	258	387	516	645
	μ	77·5	38·8	25·8	19·4	15·5
II (*c*)	cm.$^{-1}$ ..	110	220	330	440	550
	μ	90·9	45·5	30·3	22·7	17·9
II (*d*)	cm.$^{-1}$ ..	92	184	276	368	460
	μ	109	54·5	36·2	27·2	21·7

A scrutiny of the figures in Table I enables us to understand the absorptive behaviour of rock-salt in the various ranges of frequency. In the wavelength range between 13 μ and 18 μ, the absorptions that could manifest themselves are the fourth-order absorptions of modes I and II (*a*) and the fifth order absorptions of modes II (*a*), II (*b*) and II (*c*). These would necessarily be very weak and would need large absorption paths to enable them to be observed. They would also disappear quickly when the path is diminished. In the wavelength range between 18 μ and 24 μ the third-order absorptions of modes I and II (*a*) would appear, supplemented by the fourth-order absorptions of modes II (*b*) and II (*c*) and the fifth order absorptions of mode II (*d*). The strength of the third order absorptions would naturally be far greater than of those of higher orders appearing between 13 μ and 18 μ. It is, therefore, not surprising that thicknesses which allow a notable transmission in that region are completely opaque to greater wavelengths.

The vibrations of the structure responsible for the absorptions of the third, fourth and fifth orders would necessarily be of large amplitude. In consequence, the vibrations excited would be a superposition of the various normal modes approximating to each other in frequency and not the individual modes by themselves. In these circumstances, we could scarcely expect to find any observable evidence of the discreteness of the normal modes. Nonetheless, some indications of it do appear. The remarkable features noticed in the absorption curve reproduced in Fig. 8 for a thickness of 2·5 mm. may be cited as an example.

The absorptions of the second order would be far more powerful than those of the third order. Hence, much thinner layers, of the order of a hundred microns or less, would be needed to obtain any observable transmission in the region where the second-order absorptions operate. There is however much less crowding up of the normal modes. Hence it should be possible to find observational evidence of the discreteness of the absorption frequencies. The arrest in the absorption curve at about 34 μ noticed by Mentzel with rock-salt plates some 30 microns thick is clearly identifiable with the second-order absorption of mode II (*a*) listed in Table I. Likewise, the arrest extending from 40 μ to 44 μ and observed with plates 8 microns thick by Barnes and Czerny is clearly a superposition of the second-order absorptions of modes II (*b*) and II (*c*) shown in Table I.

Using evaporated films of NaCl only a few microns thick, Barnes and Czerny succeeded in obtaining an observable transmission in the spectral region where the infra-red activity is strongest and intense reflections appear. They studied the spectral character of the transmitted radiation for various

thicknesses of the films employed by them. The results which they reported, as also Czerny's observations on the variations of the reflecting power with wavelength, form a study in themselves. They are more appropriately discussed in a later part of this memoir.

SUMMARY

Infra-red activity is shown to be a consequence of the periodic movements of the electron clouds in the crystal excited by the field of the incident radiation. The accompanying oscillations of the positively charged nuclei determine the frequencies but are not themselves the cause of the activity.

It is shown that of the nine modes of free vibration of the rock-salt structure, the mode of highest frequency is intensely active both in the first and the higher orders. Four other modes are inactive in the first order but active in higher orders. The remaining four are totally inactive. Spectrographic records of the absorption of rock-salt over a wide range of thicknesses are presented and explained in terms of the activity of these modes. The results reported by Mentzel and by Barnes and Czerny on the transmission spectra of rock-salt are explained on the same basis.

THE SPECTROSCOPIC BEHAVIOUR OF ROCK-SALT AND THE EVALUATION OF ITS SPECIFIC HEAT

Part III. The Spectrum of Light Scattering

By Sir C. V. Raman

(*Memoir No.* 128 *of the Raman Research Institute, Bangalore-6*)

Received October 26, 1961

1. Introduction

In the first part of this memoir, the modes of free vibration characteristic of the structure of rock-salt were described and it was shown how their frequencies could be computed. In the second part of the memoir, the activities of these modes in the absorption and reflection of infra-red radiation were discussed. Experimental data were presented which showed clearly that the normal mode of highest frequency is active not only as a fundamental but also as overtones of higher orders. The observed infra-red behaviour of rock-salt over a wide range of frequencies of the incident radiation was discussed and explained in terms of the activities of its characteristic modes of vibration.

The present part of the memoir is concerned with an entirely different spectroscopic technique which enables the existence of the discrete normal modes of vibration to be established and their frequencies as theoretically evaluated to be checked by comparison with the results of experiment. This technique makes use of the frequency shifts observed when monochromatic light traversing the crystal emerges after diffusion in its interior and the diffused radiation is examined spectroscopically. The intensity of the radiation so diffused is a very small fraction of that traversing the crystal. But this very circumstance makes the procedure one of the highest value for the purposes in view. For, the complications which are inherent in the use of infra-red radiation in the study of the spectroscopic behaviour of such an intensely absorbing material as rock-salt are entirely avoided. The spectroscopic picture of the crystal which emerges from the recorded spectra of the diffused light is very simple, clear and definite.

We shall begin with a few remarks of a general nature. The study of the diffusion of monochromatic light by the molecules of diatomic gases,

e.g., oxygen and nitrogen, gives us an insight into the origin of the frequency shifts in light-scattering. These shifts are readily identifiable with the characteristic vibrational frequencies of the molecules. The appearance of scattered radiations of altered wavelength is thus explicable as a consequence of a periodic variation in the power of the molecule to scatter light resulting from the relative movements of its atoms in such vibration. A similar explanation can be given for the frequency shifts observed in the diffusion of light by crystals, the structural units in the crystal instead of the molecules of the gas being regarded as the vibrating systems. The structural units in a crystal are held to fixed positions and cannot move freely in the manner of the molecules in a gas. This circumstance has necessarily to be taken into account in considering the dynamics of their vibrations. But in respect of the frequency shifts arising from their internal vibrations, the randomness of phase of the scattered radiations renders the situation not essentially different from that of scattering by the individual molecules of a gas.

2. SCATTERING OF LIGHT WITH DOUBLED FREQUENCY SHIFTS

As has been remarked above, the frequency shifts observed in the scattering of light may usually be identified with the vibrational frequencies of the scattering units. There is however a remarkable class of cases in which spectral shifts are observed having double the frequency of the vibrational modes which give rise to them. We may as an illustration mention the facts emerging from a study of the scattering of light in calcite. The CO_3 groups in that crystal have four internal modes of vibration. Three of them give frequency shifts of 712 cm.$^{-1}$, 1086 cm.$^{-1}$ and 1436 cm.$^{-1}$ which may be identified respectively with the frequencies of three possible modes of vibration of the CO_3 group in its own plane. We are here concerned with a fourth frequency shift of 1749 cm.$^{-1}$ which is recorded with an intensity about equal to that of the 1436 cm.$^{-1}$ shift.

Now, the fourth mode of vibration of the CO_3 group is an out-of-plane movement in which the C atom oscillates along a line perpendicular to the O_3 group and finds itself alternately above and below the plane of the group. Such an oscillation may be expected to be strongly active in the absorption of infra-red radiation. Actually, a well-defined peak appears in the infra-red absorption spectrum of calcite at about 874 cm.$^{-1}$ and this is identified as arising from just such a vibration. But no line having that frequency shift or anywhere near it is recorded in the spectrum of the scattered light. We are thus obliged to infer that the frequency shift of 1749 cm.$^{-1}$ arises from

the infra-red active vibrational mode but is recorded in the scattering of light with double its frequency.

A doubling of the frequency shift in light-scattering as compared with an infra-red absorption frequency may be explained in the following manner. The infra-red activity arises from the movements of the electron clouds in the crystal. These movements have necessarily the same frequency as the movements of the atomic nuclei. In the scattering of light, however, we are concerned with the optical polarisability of the entire electronic cloud and this depends on its geometric configuration. In the particular case of the CO_3 group in calcite it is clear that the configuration of the group takes the same form twice in each oscillation. The periodic variation of optical polarisability has therefore twice the frequency of the vibration and hence the resulting frequency shift is also doubled. What is specially remarkable is that its intensity is comparable with those of the frequency shifts of the ordinary kind due to the other modes of vibration and that it is far greater than the intensity with which a shift of 2173 cm.$^{-1}$ (double that of the planar oscillation of 1086 cm.$^{-1}$) is recorded in the spectrum.

3. The Rock-Salt Spectrum

We proceed to show that an effect of the same general nature as that considered and explained above in the case of calcite is exhibited by all the nine normal modes of vibration of the rock-salt structure. We may begin by considering the triply degenerate mode of highest frequency which is highly active in the absorption of infra-red radiation. In this mode the sodium and chlorine nuclei with their associated electronic clouds move in opposite phases with amplitudes inversely proportional to their masses. *Twice* in each oscillation, a chlorine nucleus comes closest to a sodium nucleus either from one side or from the other. In such an approach, the power of the NaCl group to scatter light is notably increased beyond what it is when the Na and Cl nuclei are separated by their normal spacing in the crystal. Accordingly, the periodic variations of the scattering power of the NaCl groups in the crystal have *twice* the frequency of the vibrational mode. The frequency shift to which it gives rise is therefore also of double frequency. A component having the same frequency as the vibrational mode is totally absent, since the approach of a chlorine nucleus to a sodium nucleus is balanced by the recession of a chlorine nucleus from the same sodium nucleus on the opposite side. In other words, the vibrational mode is antisymmetric with respect to each sodium nucleus and each chlorine nucleus in the assembly. It is therefore inactive in light-scattering in the sense of the term as ordinarily understood.

The same argument may be extended to the four other coupled oscillations of the Na and Cl nuclei. Two of these modes are tangential and the two others normal to the cubic layers in the crystal; in all these cases, the movements in alternate layers are in opposite phases. In the tangential mode designated in the earlier parts of this memoir as II (*a*), the Na and Cl nuclei approach and recede from each other in much the same manner as in the mode I discussed above. The alternation in phase from layer to layer leaves the argument unaffected; for, at the instant when the Cl and Na nuclei are closest to each other in one layer, they would also be closest to each other in the next layer. It follows that mode II (*a*) would be active in the double-frequency modified scattering of light to much the same extent as the principal mode already considered. Indeed, mode II (*a*) having a degeneracy of six may be expected to exhibit a greater intensity than mode I which is only triply degenerate.

Considering next the tangential mode designated as II (*d*) in which the Na and Cl nuclei in each cubic layer oscillate in the same phase, the phases of the movements being reversed in the successive layers, it is evident that the double-frequency effect would also arise in respect of this mode but it would be very much feebler. For, the movements of the Na and the Cl nuclei being in the same phase, their approaches to each other would necessarily be much less close than when the movements are in opposite phases. The periodic fluctuations in the scattering power of the NaCl groups would therefore be relatively small and hence the observable effect of mode II (*d*) as recorded in the spectra of the scattered light should be far less conspicuous.

Arguments of the same kind may be extended to the consideration of the activity of the triply degenerate oscillations of the Na and Cl nuclei normal to the cubic planes designated as modes II (*b*) and II (*c*) respectively. In mode II (*b*) the Na and Cl nuclei move in the same phase and this has the higher frequency, while II (*c*) in which they move in opposite phases has the lower frequency. But the approaches between the Cl and Na nuclei which give rise to an increased scattering power are those between the nuclei which are in adjacent layers. Hence, it follows that the mode II (*b*) of the higher frequency would be much more strongly active than mode II (*c*) of the lower frequency. Since both the modes are only three-fold degenerate, their recorded intensities would be low. In particular, the mode II (*c*) of lower frequency would be recorded only very feebly.

4. ACTIVITY OF THE OCTAHEDRAL MODES

We now proceed to discuss the activity of the modes in which the Na nuclei alone, or the Cl nuclei alone oscillate. The layers containing them

are the octahedral planes of the crystal and the movement is either perpendicular or parallel to those planes, its phase being reversed in the successive layers. The oscillations perpendicular to the octahedral planes have a degeneracy of four and the nuclei move along the body-diagonals of the cube. The oscillations tangential to those planes have a degeneracy of eight and the nuclei move along one or another of the two-face diagonals appearing in the octahedral planes.

We proceed to consider the nature of the movements in these modes. In the perpendicular modes, a nucleus would approach its three nearest neighbours on the one side and recede from its three nearest neighbours on the other side. In the parallel modes, a nucleus would approach two of its nearest neighbours on one side and recede from two of its nearest neighbours on the other side. In either case, the movements would not give rise to frequency-shifts in light-scattering of the usual kind. They would, however, all be active in the modified scattering of double frequency. The parallel movements, being twice as numerous, may be expected to be recorded with greater intensity than the perpendicular ones.

We may summarise the overall picture which emerges from the foregoing considerations regarding the spectroscopic behaviour of rock-salt in light-scattering as follows:

(*a*) All the nine normal modes would exhibit a doubled frequency shift but with very different intensities.

(*b*) The triply degenerate mode of highest frequency would be strongly recorded but would be inferior in intensity to the cubic mode of lower frequency similar to it in character but which is six-fold degenerate.

(*c*) The two cubic modes of low frequency would be recorded only feebly, the one which is three-fold degenerate even more weakly than the other of lowest frequency which is six-fold degenerate.

(*d*) The eight-fold degenerate oscillation of the chlorine nuclei tangential to the octahedral planes should appear with notable intensity as a conspicuous feature in the spectrum, being adjacent to the two feebly recorded modes of lowest frequency.

(*e*) The eight-fold degenerate oscillation of the sodium nuclei parallel to the octahedral planes would be recorded more strongly than the four-fold degenerate movement perpendicular to those planes.

5. THE SPECTRUM OF LIGHT SCATTERING

The vibration frequencies of the five cubic modes involving coupled oscillations of the Na and the Cl nuclei were listed in an earlier part of this memoir. To this list we must now add the frequencies of the four octahedral modes in which only the Na or only the Cl nuclei oscillate. As a rough approximation, the frequencies of these modes can be expressed in terms of the infra-red active mode of highest frequency by replacing the reduced mass of the two nuclei in its formula by the mass of the Na nucleus alone or of the Cl nucleus alone. But, as already remarked upon and explained in the first part of the memoir, the values thus obtained need correction and their frequencies have to be increased by amounts which are greater for the perpendicular vibrations than for the parallel ones. The corrected frequencies are most conveniently determined from the spectral shifts observed in light scattering, as they are readily identified in those spectra.

TABLE I

Modes and frequencies ($cm.^{-1}$)

Modes	Degeneracy	Principal mode	Cubic class	Octahedral class	Doubled frequency	Intensity
I	3	180 (NaCl)	..	..	360	Moderate
III (*a*)	4	..	..	170 (Na)	340	Moderate
III (*b*)	8	..	..	157 (Na)	314	Strong
II (*a*)	6	..	150 (NaCl)	..	300	Strong
III (*c*)	4	..	..	140 (Cl)	280	Strong
II (*b*)	3	..	129 (NaCl)	..	258	Weak
III (*d*)	8	..	..	117·5 (Cl)	235	Intense
II (*c*)	3	..	110 (NaCl)	..	220	Very weak
II (*d*)	6	..	92 (NaCl)	..	184	Weak

Table I gives the frequencies of all the nine normal modes. Their degeneracies and descriptions are also shown. They have been entered in Table I in the descending order of frequency. The doubled frequency

shifts in light scattering appear in the penultimate column. The entry against each frequency shift under the head intensity is based on the indications of theory, *viz.*, the degeneracy of the mode and the nature of the movements involved. These considerations have already been discussed in detail above and need not therefore be repeated here.

6. The Consequences of Thermal Agitation

It is a familiar experience in studies on the scattering of light in crystals to find that the observed frequency shifts exhibit a thermal effect. The lines sharpen and the frequency shifts show a readily measurable increase when the crystal is cooled down to liquid air temperature. When, on the other hand, the crystal is warmed up, the lines become more diffuse as the result of an asymmetrical broadening. As a consequence of such broadening, the frequency shifts also diminish. The effects of this nature are both absolutely and relatively more conspicuous in the case of the vibrational modes of low frequencies. As examples may be mentioned the behaviour of calcite and of quartz in which they have been very fully studied. A thermal broadening and the accompanying diminution of the frequency shifts would necessarily occur also in the case of rock-salt. Since we are concerned with double-frequency scattering, they would be magnified two-fold. On the basis of the known data for quartz and calcite we may expect a broadening of the lines in the spectrum of rock-salt of about ten wave-numbers.

It follows from what has been stated that in the crowded spectrum indicated by the figures in Table I, the thermal broadening would result in the resolution of the frequency-shifts which are not very different becoming distinctly imperfect. When, however, a strongly recorded frequency shift has only weak companions on either side, its character as a discrete line-shift would be more clearly apparent.

7. Comparison with the Experimental Results

With a crystal of rock-salt five centimetres thick which was illuminated by the extremely intense ultra-violet radiation at λ 2536·5 emitted by a water-cooled magnet-controlled mercury arc in quartz and giving an exposure of 8 hours, Rasetti obtained a remarkable spectrogram. This was published with a microphotometer record of the spectrum alongside of it. An enlargement of this microphotometer curve copied directly from Rasetti's original publication is reproduced below as Fig. 1 in the text.

A special method was employed by Rasetti to prevent the complete fogging of the photographic plate which would have otherwise resulted from

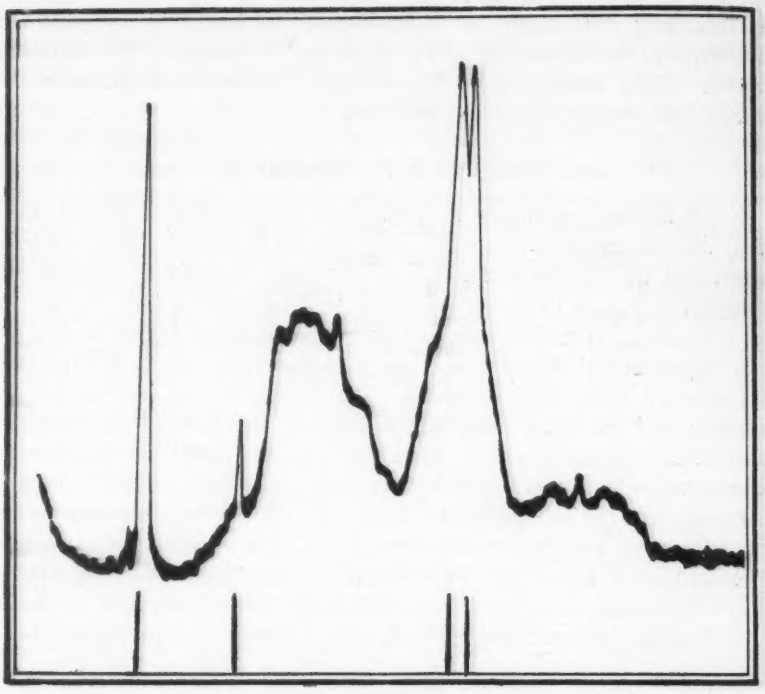

FIG. 1. Microphotometer Record (after Rasetti).

such prolonged exposure to intense illumination. A filter of mercury vapour was introduced which absorbed the 2536·5 radiation entering the instrument before it reached the photographic plate. A remarkably clear and well-exposed spectrogram was thus obtained. Neither the accompanying λ 2535 radiation nor the faint continuum extending to about 50 wave-numbers on either side of λ 2536·5 is cut out by the filter. They are recorded on the spectrogram, but have no significance.

The frequency shifts which arise from the scattering of the 2536·5 radiation in rock-salt are all found to lie between the limits 360 cm.$^{-1}$ and 184 cm.$^{-1}$ indicated by the theory. Beyond these limits, the spectrum falls off steeply in intensity. The fall on both sides would have been even steeper had the inevitable background of continuous spectrum which is an accompaniment of the monochromatic radiations of the mercury arc been totally absent in the record. But such absence could scarcely have been hoped for in view of the prolonged exposures necessary to obtain the spectrum.

For the convenience of the reader, the original spectrogram of rock-salt has been reproduced in a somewhat enlarged form as Fig. 1 in Plate VII accompanying the present memoir. On an inspection of the spectrum, it is evident that it presents precisely those features which would result from the nine double-frequency shifts listed in Table I being recorded in the positions and with the relative intensities listed in Table I. On closer examination, it becomes clear that the correspondence between the observed spectrum and the theoretical conclusions listed in Table I extends to all the observable details in it. The experimental conditions, *viz.*, the small dispersion of the spectrograph and the broadening of the frequency-shifts by the thermal agitation in the crystal are unfavourable to a complete resolution of the nine frequency shifts from each other. Nevertheless, it is clear that they are all present and have the positions and relative intensities indicated by the theory.

We may begin by referring to a striking feature in the spectrogram, *viz.*, the well-defined frequency shift of 235 cm.$^{-1}$ which stands out in the record on both sides of the exciting radiation. The shift appears in a part of the spectrum where the frequency shifts on either side are weak or very weak as indicated by the theory and also as actually observed. Naturally, therefore, the 235 cm.$^{-1}$ frequency shift is permitted to exhibit its true character as a discrete line-shift. It is not surprising also that the intensity of the shift due to the eight-fold degeneracy of the vibration makes it a prominent feature in the spectrum.

The two lowest frequencies listed in Table I are coupled oscillations of the Na and the Cl nuclei appearing in the cubic planes. The theory indicates that they would appear in the spectrum with a much lower order of intensity than the other modes, the reason being the Na and Cl nuclei have the same phase of vibration and cannot therefore make close approaches to each other. The two modes should also differ in their relative intensities by reason of the degeneracies being different, being three and six respectively. These consequences of the theory are in striking accord with the experimental facts. Actually, the frequency shifts of 220 cm.$^{-1}$ and 184 cm.$^{-1}$ are by far the feeblest recorded in the spectrum. The shift of 220 cm.$^{-1}$ is, in particular, so weak as scarcely to be visible in the reproduction of the spectrum. Its presence in the microphotometer record can be made out with some difficulty being obscured by the steep rise in the intensity as we approach the intense 235 cm.$^{-1}$ shift. The shift of 220 cm.$^{-1}$ can, however, be readily recognised in the microphotometer record on the "anti-stokes" side of the spectrum as a second and weaker hump between the 184 cm.$^{-1}$ and 235 cm.$^{-1}$ shifts. (Figure 1 in the text, right-hand side of the microphotometer curve.)

It is a significant consequence of the theory that the smaller frequency shift of 300 cm.$^{-1}$ should be recorded with twice the intensity of the larger shift of 360 cm.$^{-1}$ by reason of its higher degeneracy, though the oscillations are very similar to each other in character. That this is actually the case is clear from the spectrogram itself. In the microphotometer record (Fig. 1 in the text, left-hand side of the curve), the frequency shift of 300 cm.$^{-1}$ stands at a much higher level than 360 cm.$^{-1}$ It is well known, however, that differences in intensity between the different lines in a spectrogram are better appreciated when the exposure is not very heavy, as the photographic blackening is then not too great to show up the gradations in exposure. Likewise, for a microphotometer record, a moderately exposed plate is more suitable than a heavily exposed one. For, in the latter case, the differences of intensity are greater reduced in the transmission through the blackened plate which is recorded photometrically.

The importance of the foregoing remarks will be realised on an examination of the microphotometer record reproduced above in the text as Fig. 1. Rasetti's spectrogram and its microphotometer trace show the spectral shifts recorded on both sides of the exciting radiation λ 2536·5. On the " anti-stokes " side, the exposures are much less heavy and hence its microphotometric record is better suited to exhibit the relations of intensity between adjacent parts of the spectrum than the record of the more heavily exposed spectrum on the other side.

It has been already remarked that the 220 cm.$^{-1}$ shift which is only vaguely indicated on the heavily exposed side of the record is quite clearly seen on the " anti-stokes " side. Likewise, all the frequency shifts listed in Table I are clearly visible on the " anti-stokes " side of the microphotometer record distinctly separated from each other. Instead of the 360 cm.$^{-1}$ and 340 cm.$^{-1}$ shifts appearing fused into a single band as on the heavily exposed side, they are seen on the " anti-stokes " side quite clearly as two distinct steps one above the other. The third step which is visible in the record is the 314 cm.$^{-1}$ shift. Two other strongly recorded shifts, *viz.*, 300 cm.$^{-1}$ and 280 cm.$^{-1}$, are seen higher up in the photometer curve. The weak 258 cm.$^{-1}$ shift appears as the drop in intensity which immediately precedes the strongly recorded peak shift of 235 cm.$^{-1}$ Thus, the microphotometer record on the " anti-stokes " side enables us to recognise all the nine frequency shifts individually and to appreciate the great differences in intensity which they present more clearly than the record on the heavily exposed side permits.

We may sum up the foregoing by stating that the experimental results completely establish the correctness of our theoretical approach and are a

verification of the various observable consequences to which the theory points.

8. Summary

All the nine normal vibrational modes of the rock-salt structure can give frequency shifts in light-scattering which are twice their respective frequencies but are of very different intensities, determined by their degeneracies and the nature of the movements of the Na and Cl nuclei in those modes. The doubled frequencies in cm.$^{-1}$ with their respective degeneracies are 360 (3), 340 (4), 314 (8), 300 (6), 280 (4), 258 (3), 235 (8), 220 (3), 184 (6). The spectroscopic facts are in full agreement with the theoretical deductions.

APPENDIX

Reflection and Transmission of Long Waves

The frequencies of the characteristic vibrational modes of the rock-salt structure determined spectroscopically and expressed as infra-red wavelengths are the following: $55{\cdot}6\,\mu$, $58{\cdot}8\,\mu$, $63{\cdot}7\,\mu$, $66{\cdot}7\,\mu$, $71{\cdot}4\,\mu$, $77{\cdot}5\,\mu$, $85{\cdot}0\,\mu$, $90{\cdot}9\,\mu$ and $108\,\mu$. The question arises of the part they play in the reflection by rock-salt surfaces and in the transmission through thin films of long-wave infra-red radiation.

Amongst these modes, that of the highest frequency with the characteristic wavelength $55{\cdot}6\,\mu$ stands in a class apart by itself, being the strongly infra-red active fundamental. It is therefore to be expected that this mode would play a dominating role in the reflection of infra-red radiation and that it would also menifest itself as the principal cause of absorption in thin films.

The reflecting power of rock-salt actually reaches its maximum value of about 90% at a wavelength which is nearly the same as that of its active fundamental. But it is considerable both at shorter and at longer wavelengths. On the long wavelength side, the reflecting power diminishes progressively and reaches a limiting value of 20% at and beyond $100\,\mu$. On the short wavelength side, the reflecting power drops off more quickly and becomes quite small at about $33\,\mu$. There are indications of a minor maximum of reflecting power at about $38\,\mu$.

That the reflecting power at shorter wavelengths is considerable is readily explained. Four of the characteristic vibrational modes are coupled oscillations of the Na and the Cl nuclei in the crystal which are strongly infra-red active with a *doubled frequency*. The absorption wavelengths thus arising are $33{\cdot}3\,\mu$, $38{\cdot}8\,\mu$, $45{\cdot}5\,\mu$ and $54{\cdot}3\,\mu$ respectively. The existence of absorptions at these wavelengths is indeed demonstrable by observations with rock-salt plates with appropriately chosen thicknesses. Their co-operation with the active fundamental in infra-red reflection is a natural consequence. That the reflecting power becomes negligible at wavelengths less than $33\,\mu$ is only to be expected in these circumstances.

The existence of a whole series of normal modes of vibrations of the rock-salt structure with characteristic wavelengths ranging between $55\,\mu$ and $108\,\mu$ furnishes us with a clue to the explanation of the fact that the reflecting power of rock-salt diminishes only slowly in this range and reaches its

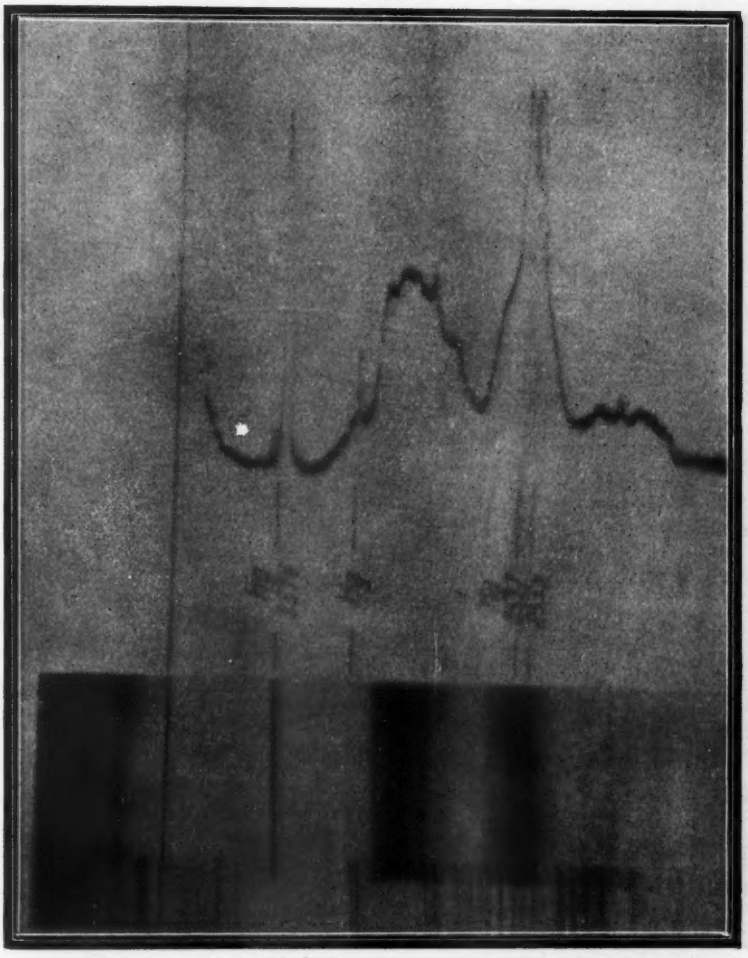

FIG. 1. Double-Frequency Shifts in Light-Scattering by Rock-Salt.

limiting value of 20% beyond 100 μ. Infra-red activity arises from the movements of the electronic clouds in the crystal set up by the incident radiation. A complete independence of the normal modes of vibration and of their excitation cannot be assumed in these circumstances. That the different normal modes would co-operate to varying extents and that such excitation would manifest itself in the reflecting power of the crsytal is only to be expected.

In determining the transmission by the thinnest films of NaCl, the fundamental absorption at 55·6 μ would naturally play the leading role. But one cannot ignore the existence of other absorptions which would simultaneously operate. Amongst these are the modes which are active with doubled frequencies as stated above. We should also take account of the whole series of modes with greater wavelengths which may be simultaneously excited by the reason of the non-independence of normal modes. It would not be surprising if in these circumstances the wavelength of maximum absorption is shifted appreciably towards wavelengths greater than 55·6 μ.

THE SPECTROSCOPIC BEHAVIOUR OF ROCK-SALT AND THE EVALUATION OF ITS SPECIFIC HEAT

Part IV. Specific Heat and Spectral Frequencies

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(*Memoir No.* 128 *of the Raman Research Institute, Bangalore-6*)

Received October 28, 1961

1. Introduction

The numerous published measurements of the thermal energy-content of crystalline solids and its variation with temperature make it clear that the theory of specific heats is concerned with the movements of the atomic nuclei in crystals about their positions of equilibrium and especially with the frequencies of their vibrations. A clear picture of the nature of these vibrations emerges if we take the basic facts of crystal architecture as our starting point, *viz.*, that a crystal consists of an immense number of similar and similarly situated units of structure. Each unit of structure contains a group of atomic nuclei which can interact with each other through the electrons which hold them together. The next step is to make use of the theory of small vibrations in classical mechanics to find the normal modes and frequencies of free vibration of these nuclei about their positions of equilibrium. In treating this problem, we have of necessity to recognise and take account of the three-dimensional periodicity of the crystal architecture. The principles of thermodynamics and of the quantum theory have then to be introduced and applied to the problem. They indicate that the normal modes deduced classically would be excited to various levels of energy, the relative probabilities of such excitation being determined by the respective energies and the absolute temperature. The average energy associated with each such normal mode and hence also the total average energy of all the normal modes taken together can then be computed. A multiplication of this average by the number of the oscillators in the crystal considered gives the total thermal energy of the solid as a function of the temperature.

It has been shown in the preceding parts of this memoir that a basically similar approach enables us to explain or elucidate the spectroscopic properties of the crystal. It follows that the thermal and spectroscopic behaviours

of the crystal stand in the closest relationship to each other. It should therefore be possible by making use of the spectroscopically determined frequencies of vibration to evaluate the specific heat of the crystal as a function of temperature and proceed to a comparison of the results thus obtained with the measured specific heats. No data are required for such an evaluation except those emerging from the spectroscopic studies. It follows that an agreement between theory and experiment would constitute a perfect demonstration of the correctness of the approaches made alike to spectroscopic theory and to the theory of specific heats.

2. The Spectral Frequencies of Rock-Salt

In the case of magnesium oxide which has been dealt with in memoir No. 127 appearing in the same issue of these *Proceedings*, the spectroscopic frequencies were determined by the study of infra-red absorption in that crystal. In the case of rock-salt now considered, we have two distinct methods of investigation available which, as has already been noticed, give results supporting each other and confirming the inferences from theory. Of the two methods of study, *viz.*, infra-red spectroscopy and the scattering of light, the latter is definitely superior, since the data furnished by it are both complete and exact. All the nine modes appear in light-scattering with doubled frequency shifts with respect to the position in the spectrum of the $\lambda 2536{\cdot}5$ radiation of the mercury arc used to illuminate the crystal. The spectral shifts are recorded on both sides of the exciting radiation, and the microphotometer records of the spectrum on the two sides usefully supplement each other. On the heavily exposed side, the background due to the continuous radiation in the incident light is relatively less important, and the record therefore gives a truer picture of the spectrum taken as a whole. But, on the other hand, the heavy exposure results in obscuring finer detail and its microphotometer record fails to exhibit a complete resolution of the spectrum into its distinct components. The microphotometric record of the weakly exposed side is greatly superior in this respect. Not only does it reveal the nine distinct double-frequency shifts in the scattered light but also enables them to be read off directly from the record with tolerable accuracy.

Figure 1 in the text is the same record as that reproduced as Fig. 1 in the previous part of the memoir. But now the frequency shifts have been entered and shown against the visible peaks in the record which enabled them to be measured with reference to the position of the exciting radiation, the prominent 235 $cm.^{-1}$ shift being used to furnish the necessary scale of frequencies. The frequency shifts determined in this manner and entered

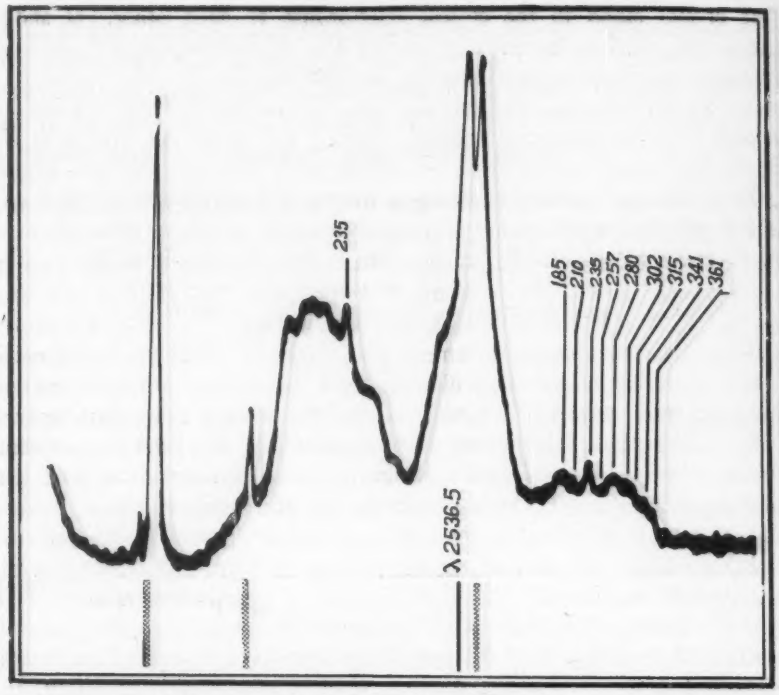

FIG. 1. Microphotometer Record showing frequency shifts.

in the figure differ little from those obtained by measurements under a micrometer of original spectrum plates recorded with rock-salt.

3. COMPARISON WITH THE SPECIFIC HEAT DATA

The manner in which we proceed from the spectroscopic frequencies to evaluate the specific heat of rock-salt as a function of the temperature is entirely analogous to that already fully explained for the case of MgO in a memoir appearing in the same issue of these *Proceedings*. It is unnecessary to traverse the ground here once again and it suffices to present a tabulation of the contributions to the specific heat made by the different normal modes of vibration, as also by the residual spectrum of vibration frequencies which is continuous and extends towards zero frequency. The normal frequencies of vibration made use of in the calculations are one-half the frequency shifts (in $cm.^{-1}$) observed in the scattering of light.

Though the structure of rock-salt is similar to that of MgO, the two cases differ in certain important respects. The vibration spectrum of rock-

salt lies much further out in the infra-red than that of MgO. As is to be expected in the circumstances, the increase in its specific heat from very low to normal values takes place for the most part in the region of liquid air and liquid hydrogen temperatures. Tabulations are therefore required in the case of rock-salt only for temperatures between 0 and 300 degrees absolute.

The foregoing remarks have some further implications. As has been pointed out in the third part of this memoir, the frequency shifts observed in light scattering exhibit a temperature effect. The frequency shifts broaden asymmetrically and also move to smaller values as the temperature is raised. In the case of rock-salt, the spectroscopic data we make use of were obtained with the crystal held at room temperature. Hence, it cannot be expected that these data would fit the specific heat curve at very low temperatures and especially at the tempeartures where the specific heat changes most rapidly. We could only expect the theoretically calculated specific heats for low temperatures to agree with observed specific heats if the frequencies used had been determined with the crystal held at the same temperatures.

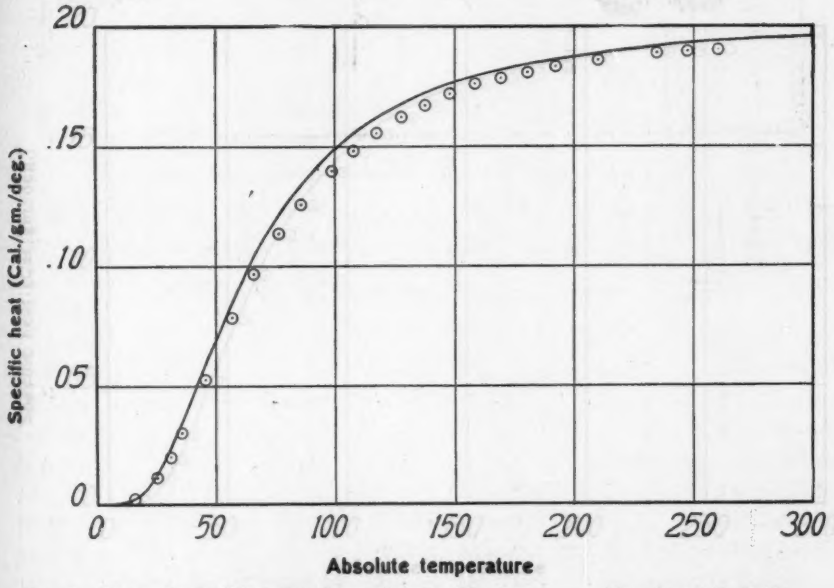

FIG. 2. Comparison of theory and experiment. Theory ——. Experiment ⊙⊙⊙.

The foregoing remarks find support in the results of the actual computations. Tables I and II show the specific heats as computed and the

TABLE I

Computation of the specific heats

	10° K	15° K	25° K	50° K	75° K	100° K	125° K
$3E_1$ (180 cm.$^{-1}$)	..	..	0·0023	0·1088	0·2929	0·4312	0·5223
$4E_2$ (170 cm.$^{-1}$)	..	..	0·0047	0·1738	0·4278	0·6091	0·7235
$8E_3$ (157 cm.$^{-1}$)	..	0·0001	0·0176	0·4359	0·9638	1·3059	1·5135
$6E_4$ (150 cm.$^{-1}$)	..	0·0001	0·0181	0·3673	0·7652	1·0137	1·1610
$4E_5$ (140 cm.$^{-1}$)	..	0·0002	0·0188	0·2876	0·5545	0·7099	0·7994
$3E_6$ (129 cm.$^{-1}$)	..	0·0004	0·0226	0·2571	0·4517	0·5593	0·6180
$8E_7$ (118 cm.$^{-1}$)	..	0·0026	0·0960	0·8042	1·3013	1·5608	1·6985
$3E_8$ (110 cm.$^{-1}$)	..	0·0019	0·0502	0·3362	0·5154	0·6043	0·6506
$6E_9$ (92 cm.$^{-1}$)	0·0004	0·0156	0·2056	0·8453	1·1482	1·2852	1·3569
3D (92 cm.$^{-1}$)	0·0240	0·0767	0·2458	0·5332	0·6378	0·6818	0·7036
Molecular heat (cal./gm./deg.)	0·0244	0·0976	0·6817	4·1494	7·0586	8·7612	9·7473
Specific heat (cal./gm./deg.)	0·0004	0·0017	0·0117	0·0710	0·1208	0·1499	0·1668

TABLE II

Computation of the specific heats

	150° K	175° K	200° K	225° K	250° K	275° K	300° K
$3E_1$ (180 cm.$^{-1}$)	0·5805	0·6195	0·6468	0·6647	0·6805	0·6909	0·6983
$4E_2$ (170 cm.$^{-1}$)	0·7952	0·8416	0·8738	0·9005	0·9156	0·9283	0·9377
$8E_3$ (157 cm.$^{-1}$)	1·6398	1·7249	1·7807	1·8229	1·8510	1·8753	1·8927
$6E_4$ (150 cm.$^{-1}$)	1·2507	1·3084	1·3528	1·3776	1·3965	1·4125	1·4248
$4E_5$ (140 cm.$^{-1}$)	0·8530	0·8863	0·9114	0·9269	0·9390	0·9487	0·9554
$3E_6$ (129 cm.$^{-1}$)	0·6542	0·6774	0·6920	0·7023	0·7106	0·7166	0·7204
$8E_7$ (118 cm.$^{-1}$)	1·7807	1·8340	1·8673	1·8903	1·9087	1·9211	1·9326
$3E_8$ (110 cm.$^{-1}$)	0·6785	0·6941	0·7063	0·7141	0·7197	0·7241	0·7274
$6E_9$ (92 cm.$^{-1}$)	1·3945	1·4178	1·4347	1·4455	1·4535	1·4599	1·4644
3D (92 cm.$^{-1}$)	0·7159	0·7229	0·7281	0·7314	0·7338	0·7357	0·7370
Molecular heat	10·3430	10·7269	10·9939	11·1762	11·3089	11·4131	11·4907
Specific heat (cal./gm./deg.)	0·1770	0·1835	0·1881	0·1912	0·1935	0·1953	0·1966

TABLE III

Computation of the specific heats

	10° K	15° K	25° K	50° K	75° K	100° K	125° K
$3E_1$ (189 cm.$^{-1}$)	..	..	0·0015	0·0925	0·2678	0·4058	0·5034
$4E_2$ (179 cm.$^{-1}$)	..	..	0·0031	0·1478	0·3944	0·5794	0·6986
$8E_3$ (165 cm.$^{-1}$)	..	0·0001	0·0121	0·3804	0·8966	1·2504	1·4693
$6E_4$ (158 cm.$^{-1}$)	..	0·0001	0·0125	0·3212	0·7165	0·9725	1·1318
$4E_5$ (147 cm.$^{-1}$)	..	0·0001	0·0138	0·2576	0·5233	0·6872	0·7804
$3E_6$ (135 cm.$^{-1}$)	..	0·0002	0·0175	0·2339	0·4312	0·5443	0·6073
$8E_7$ (124 cm.$^{-1}$)	..	0·0017	0·0749	0·7360	1·2504	1·5223	1·6715
$3E_8$ (116 cm.$^{-1}$)	..	0·0012	0·0392	0·3104	0·4949	0·5901	0·6412
$6E_9$ (97 cm.$^{-1}$)	0·0002	0·0106	0·1674	0·7949	1·1153	1·2624	1·3416
3D (97 cm.$^{-1}$)	0·0204	0·0665	0·2213	0·5146	0·6270	0·6746	0·6991
Molecular heat	0·0206	0·0805	0·5633	3·7893	6·7174	8·4890	9·5442
Specific heat (cal./gm./deg.)	0·0004	0·0014	0·0096	0·0648	0·1149	0·1452	0·1633

TABLE IV

Computation of the specific heats

	150° K	175° K	200° K	225° K	250° K	275° K	300° K
$3E_1$ (189 cm.$^{-1}$)	0·5659	0·6073	0·6370	0·6566	0·6754	0·6856	0·6941
$4E_2$ (179 cm.$^{-1}$)	0·7761	0·8280	0·8625	0·8883	0·9087	0·9213	0·9323
$8E_3$ (165 cm.$^{-1}$)	1·6113	1·6985	1·7603	1·8092	1·8397	1·8620	1·8833
$6E_4$ (158 cm.$^{-1}$)	1·2268	1·2909	1·3355	1·3672	1·3883	1·4045	1·4178
$4E_5$ (147 cm.$^{-1}$)	0·8397	0·8754	0·9046	0·9213	0·9337	0·9440	0·9522
$3E_6$ (135 cm.$^{-1}$)	0·6468	0·6708	0·6878	0·6983	0·7071	0·7133	0·7181
$8E_7$ (124 cm.$^{-1}$)	1·7572	1·8201	1·8567	1·8833	1·9020	1·9149	1·9273
$3E_8$ (116 cm.$^{-1}$)	0·6708	0·6888	0·7013	0·7106	0·7166	0·7212	0·7254
$6E_9$ (97 cm.$^{-1}$)	1·3840	1·4105	1·4283	1·4409	1·4495	1·4574	1·4621
3D (97 cm.$^{-1}$)	0·7126	0·7207	0·7261	0·7300	0·7326	0·7350	0·7364
Molecular heat	10·1912	10·6110	10·9001	11·1057	11·2536	11·3592	11·4490
Specific heat (cal./gm./deg.)	0·1744	0·1815	0·1865	0·1900	0·1925	0·1943	0·1959

TABLE V

Experimental data of specific heats

Temperature	10·9° K	15·3° K	25·1° K	50·7° K	76·4° K	103·1° K
Molecular heat ..	0·044	0·134	0·658	3·820	6·626	8·424
Specific heat .. .. .. (cal./gm./deg.)	0·0008	0·0023	0·0113	0·0654	0·1134	0·1441

Temperature	127·7° K	153·2° K	174·9° K	198·1° K	222·5° K	253·9° K	260·6° K
Molecular heat ..	9·486	10·162	10·542	10·792	11·006	11·104	11·134
Specific heat .. (cal./gm./deg.)	0·1623	0·1739	0·1804	0·1846	0·1883	0·1900	0·1905

(Experimental values of specific heat of NaCl taken from K. Clusius, J. Goldmann and A. Perlick, *Z. Naturforschg*, 1949, 4 A, 424–432.)

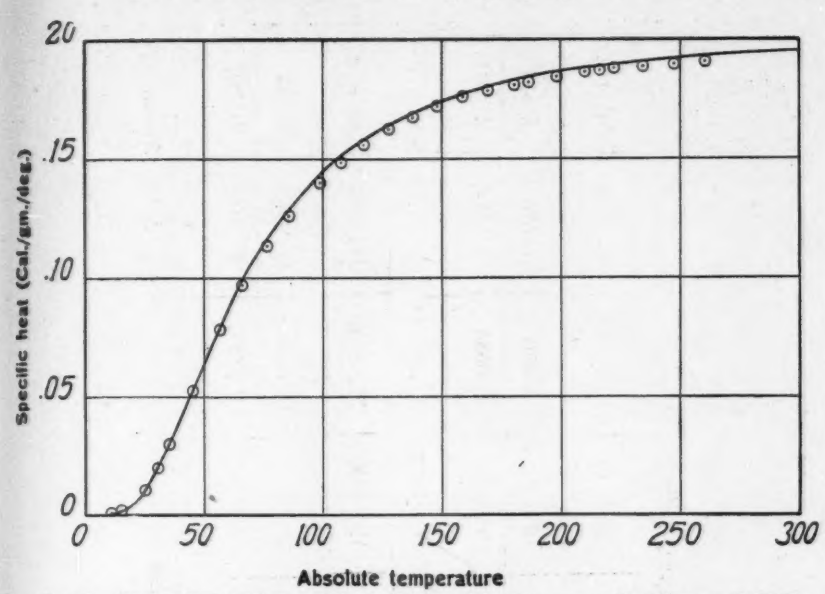

FIG. 3. Comparison of theory and experiment. Theory ——. Experiment ⊙⊙⊙.

results have been drawn as a continuous graph in Fig. 2 in the text. The experimental values in the same range of temperatures are given in Table V and have been shown as dotted circles in Fig. 2. It will be seen that the experimental values lie systematically below the theoretical curve, the deviations being greatest in the range between 50 and 150 degrees absolute.

The differences between theory and experiment indicated in Fig. 2 arise, without doubt, by reason of the spectroscopic frequencies used in the calculations being less than the actual spectroscopic frequencies at low temperatures. Precisely what the latter are cannot be stated on the basis of present knowledge. Any attempt to fit theory and experiment by using assumed values for the frequencies might well be thought artificial and unsatisfactory. It appeared however useful to present a second set of computations in which all the frequencies made use of are raised uniformly by 5% of their respective values. Such an increase is certainly not greater than would be justified by a comparison with those cases, *e.g.*, quartz and calcite, where the effect of using liquid air temperatures on the vibration frequencies has been quantitatively studied. The fresh computations on this basis have been shown in Tables III and IV, and their results plotted in Fig. 3 against the experimental results. The greatly improved agreement between theory and experiment which is exhibited in Fig. 3 makes it clear

that the lack of such agreement appearing in Fig. 2 is due to the frequencies made use of in that case not being the actual frequencies. Indeed, a perfect fit with the experimental data could have been obtained by appropriate alterations in the frequencies made use of in the calculations. But it did not appear worthwile to attempt to do this for the reason that Figs. 2 and 3 by themselves make it perfectly clear that the approach to the specific heat theory made in the present investigation is essentially a complete success.

4. SUMMARY

The spectroscopically determined vibration frequencies of the rock-salt structure are made use of for a theoretical evaluation of its specific heat as a function of temperature. The results thus obtained are compared with the measured specific heats. The agreement between theory and experiment which emerges demonstrates the correctness of the approaches made alike to spectroscopic theory and to the theory of specific heats.

795–61. Printed at the Bangalore Press, Bangalore City, by T. K. Palakrishnan, Superintendent, and Published by The Indian Academy of Sciences, Bangalore.

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CONTENTS

PAGE

The Vibrations of the MgO Crystal Structure and Its Infra-Red Absorption Spectrum. Part I. The Results of Experimental Study . . . . . Sir C. V. Raman 205

The Vibrations of the MgO Crystal Structure and Its Infra-Red Absorption Spectrum. Part II. Dynamical Theory . . . Sir C. V. Raman 223

The Vibrations of the MgO Crystal Structure and Its Infra-Red Absorption Spectrum. Part III. Comparison of Theory and Experiment . . . . . Sir C. V. Raman 233

The Vibrations of the MgO Crystal Structure and Its Infra-Red Absorption Spectrum. Part IV. Evaluation of Its Specific Heat . . . . . Sir C. V. Raman 244

The Spectroscopic Behaviour of Rock-Salt and the Evaluation of Its Specific Heat. Part I. The Structure and Its Free Vibrations Sir C. V. Raman 253

The Spectroscopic Behaviour of Rock-Salt and the Evaluation of Its Specific Heat. Part II. Its Infra-Red Activity . . . . Sir C. V. Raman 266

The Spectroscopic Behaviour of Rock-Salt and the Evaluation of Its Specific Heat. Part III. The Spectrum of Light Scattering Sir C. V. Raman 281

The Spectroscopic Behaviour of Rock-Salt and the Evaluation of Its Specific Heat. Part IV. Specific Heat and Spectral Frequencies . . . . . Sir C. V. Raman 294